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The Iron Oxides

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The Iron Oxides

Structure, Properties, Reactions,
Occurrences and Uses

Second, Completely Revised and Extended Edition



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1st Edition 1996

1st Reprint 1997

2nd Reprint 1998

2nd Edition 2003

Cover Illustration

Prehistoric cave painting of a red horse from Lascaux. The colours used in the painting were obtained from the local deposits of red and yellow ochres, i.e. iron oxides. Similar ochre deposits in Southern France are still mined for pigment production today. As colouring agents, iron oxides have served man more or less continuously for over 30,000 years. A major, modern technological application of these compounds (mainly in synthetic form) is as pigment.
(Courtesy of Musée National de Préhistoire Les Eyzies).

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Library of Congress Card No.: Applied for:

British Library Cataloguing-in-Publication

Data: A catalogue record for this book is available from the British Library.

Bibliographic information published by

Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>.

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

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Printed on acid-free paper

Composition ProSatz Unger, Weinheim

Printing Druckhaus Darmstadt, Darmstadt

Bookbinding Litges & Dopf, Heppenheim
Printed in the Federal Republic of Germany

ISBN 3-527-30274-3

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Preface to the Second Edition

Since this book first appeared, there have been hundreds of new publications on the subject of iron oxides. These have covered a wide range of disciplines including surface chemistry, the geosciences, mineralogy, environmental science and various branches of technology. In view of the amount of new material that is available, we decided, that once the copies of the first edition were exhausted, we would prepare a second edition that would incorporate the new developments.

As before, our aim has been to bring all aspects of the information concerning iron oxides into a single, compact volume. All the chapters have been revised and updated and new figures and tables added. The book is structured according to topic with the same arrangement as in the first edition being followed. In view of the recent recognition of the impact iron oxides have on environmental processes, a chapter dealing with the environmental aspects of these compounds has been added. The book concludes with a considerably expanded bibliography.

We hope that this new edition will continue to be of interest to all those researchers who, in one way or another, are involved with iron oxides.

Numerous persons and institutions from around the world again supplied data, figures, colour pictures and electron micrographs and technical help. These include Dr. H. Chr. Bartscherer (München), Mr M. Burlot (Apt), Dr. R. Bäumlér and Dr. Becher (Freising), Mr H. Breuning (Stuttgart), Dr. J. M. Bigham (Columbus, USA), Dr. G. Buxbaum (Bayer), Dr. L. Carlson (Helsinki), Dr. R. A. Eggleton (Canberra), Dr. F. G. Ferris (Toronto), Dr. R. W. Fitzpatrick (Adelaide), Dr. D. Fortin (Ottawa), Dr. M. R. Fontes (Guatemala), Professor R. Giovanoli (Bern), Dr. G. Glasauer (Guelph), Dr. M. Hanslick (München), Dr. P. Jaesche (Freising), Dr. A. A. Jones (Reading), Dr. R. C. Jones (Honolulu), Dr. D. E. Janney (Tempe), Dr. R. Loeppert (College Station), Professor S. Mann (Bristol), Dr. E. Murad (Marktreidwitz), Dr. H. Maeda (Tsukuba), Professor A. Manceau (Grenoble), Professor E. Matijevic (Potsdam, USA), Mrs U. Maul (Freising), Dr. J. P. Muller (Paris), Musée National de Préhistoire (Les Eyzies, France), Mr R. Miehler (München), Dr. T. Nagano (Naka), Dr. H. Naono (Uegahara), NASA (Houston), Professor A. Posner † (Perth), Mrs M. Sauveté (Apt), Dr. N. Sabil (München), Dr. P. Schad (Freising), Dr. A. Scheidegger (Zürich), Dr. T. Schwarz (Berlin), Dr. A. Scheinost (Zürich), Dr. D. Schüler (Bremen), D. Schwertmann (Freising), Professor H. Stanjek (Aachen), Dr. P. Self (Adelaide), Professor T. Sugimoto (Sendai), Dr. K. Tazaki (Ishikawa), Dr. T. Tessier

(Versailles), Professor C. F. Tietz (Hamburg), Professor J. Torrent (Cordoba), Dr. H. Vali (Montreal), Dr. E. Tronc (Paris).

Our warm thanks go to all these people.

One of us (U.S.) thanks Professor Kogel-Kuabner for permission to use the facilities of The Soils Department in Weiheinstephan and Dr. H. Becker and other colleagues in this institute for advice and assistance in the use of the computer.

Finally, we should like to thank the staff of Wiley-VCH for their patience and cooperation in the production of this book.

May 2003

R. M. Cornell
U. Schwertmann

Preface to the First Edition

Iron oxides have served man for centuries. Since the red and yellow ochres were first used to help produce prehistoric paintings in caves such as those at Lascaux, the role of iron oxides has expanded enormously. Their application as pigments and their ability to catalyse various chemical reactions, their role as the precursors of iron and steel and their activity as adsorbants in the ecosphere are just a few examples of the contribution of these compounds to the well-being of man.

As long ago as 1937, Fricke and Hüttig reviewed the state of the art regarding metal oxides in “Hydroxyde und Oxydhydrate”, a book in which 50 pages were devoted to those of iron. To the best of our knowledge, no review of this topic has appeared since. This is surprising in view of the immense amount of research activity and information concerning iron oxides which has accumulated in recent decades. As shown in Chapter 1, workers from a range of different disciplines are interested in these compounds. Recently developed techniques such as EXAFS, AFM and STM are being applied to elucidate details of the interior and surfaces of iron oxides. Owing to the small size (nm range) and degree of disorder in many iron oxide crystals, only these modern techniques have the capacity to provide the information necessary for understanding of the behaviour of these compounds. The data from all these investigations are distributed over publications in diverse journals with the result that workers in one field are often unaware of development in other areas.

This book is aimed at collecting all aspects of the information about iron oxides into one compact volume. It provides a coherent text with a maximum of homogeneity and minimum overlap between chapters. It is structured according to topics, i. e. surface chemistry, dissolution behaviour, adsorption etc. For each topic a general introduction is followed by a section which reviews current knowledge concerning the different iron oxides. The latter section includes much detailed information and recent data from the authors' own laboratories. As this is intended to be a handbook, an extensive list of references to help the reader expand various details is provided. We have also indicated some of the numerous opportunities for further research in this field.

The book is intended for those researchers who, whatever their discipline, are working with iron oxides. We hope it will be of use to these representatives of extremely diverse fields who are linked by their common interest in this fascinating group of compound.

Acknowledgements

In compiling this book we received substantial help from a large number of people.

Professor R. Giovanoli (Universität Bern) was invaluable in reading and commenting on various chapters, supplying electron micrographs and other data and in discussing various matters. Our warmest thanks to Dr. H. Stanjek (Technische Universität, München) for reviewing different chapters, for discussion and for contributions. He also produced new computer drawings of the structure models of the Fe oxides. We are indebted to various other colleagues for reading certain chapters, for helpful comments and for valuable additions. These include Dr. G. Buxbaum (Bayer AG, Krefeld), Dr. J. W. E. Faßbinder (Bayer. Landesamt für Denkmalpflege, München), Dr. S. Glasauer (University of California, Berkeley), Dr. A. Hugot-LeGoff (Université P. and M. Curie, Paris), Dr. S. G. McMillan (University of Otago, Dunedin, N.Z.), Dr. E. Murad (Bayer. Geol. Landesamt, Bamberg), Professor P. W. Schindler (Universität Bern), Professor W. Schneider (ETH, Zürich) and Dr. P. Weidler (ETH, Zürich).

Numerous persons and institutions kindly contributed colour illustrations, pictures, electron micrographs and other data. These include Dr. H. Chr. Bartscherer (München), Bayer AG (Krefeld), Dr. J. M. Bigham (Columbus), Dr. L. Carlson (Helsinki), Dr. R. A. Eggleton (Canberra), Dr. R. W. Fitzpatrick (Adelaide), Dr. M. R. Fontes (Guatemala), Dr. J. Friedl (Freising), Dr. J. Gerth (Hamburg), Dr. A. A. Jones (Reading), Dr. R. C. Jones (Honolulu), Professor G. Lagaly (Kiel), Dr. R. Loeppert (College Station, USA), Professor S. Mann (Bath), Professor E. Matijevic (Potsdam, USA), Dr. J. P. Muller (Paris), the Musée National de Préhistoire (Les Eyzies, France), Dr. H. Naono (Uegahara), NASA (Houston), Parc Naturel Regional du Luberon (France), Dr. A. Posner † (Perth), Dr. A. Scheidegger (Zürich), Dr. T. Schwarz (Berlin), D. Schwertmann (Freising), Dr. P. Self (Adelaide), Dr. D. Tessier (Versailles), Professor G. F. Tietz (Hamburg), Professor J. Torrent (Cordoba), Dr. H. Vali (Montreal), Professor J. van Landuyt (Antwerp), Dr. T. R. Walker (Denver) and Dr. P. Weidler (Zürich). Thanks are due to Dr. A. Middleton (British Museum, London) for information and publications.

We gratefully acknowledge the excellent work put in by the staff at the Institut für Bodenkunde (Technische Universität München at Freising) particularly Mrs. E. Schuhbauer for her unflagging interest and splendid computer draftmanship and to Mrs. B. Zarth and Mrs. M. Schwarz for their meticulous attention to detail in typing the text, assembling tables and references and eliminating errors; it was certainly not an easy task. In the initial stage of the book Mrs. C. Stanjek supplied technical help.

The wonderful cooperation of all these people has been invaluable. Our sincere thanks goes to all of them. Finally we thank VCH for their support and outstanding patience during this period.

Perth and Freising, July 1996

*R. M. Cornell
U. Schwertmann*

Abbreviations

AES	Auger electron spectroscopy
AFM	atomic force microscopy
Ak	akaganéite
ASTM	American Society for Testing and Materials
ATP	adenosine triphosphate
ATR	attenuated total reflectance
bcc	body-centred cubic
BCF	Burton-Cabrera-Frank mechanism
bcp	body centered (close) packing
BET	Brunauer, Emmett and Teller
BIF	banded iron formation
BM	Bohr magneton
CCC	critical coagulation concentration
ccp	cubic close packing
CDTA	cyclohexylene dinitrilo tetraacetic acid
CFSE	crystal field stabilization energy
CIE	Commission Internationale de l'Eclairage
CIR	cylindrical internal reflectance
CSIRO	Commonwealth Scientific Industrial Research Organization
DCB	dithionite-citrate-bicarbonate
DDL	diffuse double layer
DLVO	Derjaguin, Landay, Verwey and Overbeek
DRS	diffuse reflectance spectroscopy
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTPA	diethylene triamine pentaacetic acid
ED	electron diffraction
edl	electrical double layer
EDTA	ethylene diamine tetra acetic acid
EGME	ethylene glycol monoethylether
EPR	electron paramagnetic resonance spectroscopy
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
FAO	Food and Agriculture Organization
Fh	ferrihydrate
FTIR	Fourier-transform-infrared (spectroscopy)
GR	green rust
Gt	goethite
hep	hexagonal close packing
HFO	hydrous ferric oxide

Hm	haematite
HRTEM	high resolution transmission electron microscopy
HS	high spin
IAP	ion activity product
iep	isoelectric point
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
LEED	low energy electron diffraction
LOI	loss on ignition
Lp	lepidocrocite
LS	low spin
M	metal
MCL	mean coherence length
MD	multidomain
Mh	maghemite
MIO	micaceous iron oxide
Mt	magnetite
MW	molecular weight
NMR	nuclear magnetic resonance
NTA	nitrilotriacetic acid
ppzc	pristine point of zero charge
PS	photoelectron spectroscopy
PSD	pseudo single domain
pzc	point of zero charge
pznpc	point of zero net proton charge
pzse	point of zero salt effect
RR	redness rating
RT	room temperature
RTP	room temperature and pressure
SAD	selected area diffraction
SAXS	small-angle-X-ray-scattering
SD	single domain
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SIMS	secondary ion imaging mass spectroscopy
SIRM	saturation isothermal remanent magnetization
SP	superparamagnetic
STM	scanning tunnelling microscopy
STP	standard temperature and pressure
TEA	triethanolamine
TEM	transmission electron microscopy
TGA	thermal gravimetric analysis
UV-Vis	ultraviolet-visible
WHH	width at half height
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1

Introduction to the iron oxides

Iron oxides are common compounds which are widespread in nature and readily synthesised in the laboratory. They are present in almost all of the different compartments of the global system: atmosphere, pedosphere, biosphere, hydrosphere and lithosphere and take part in the manifold interrelationships between these compartments as shown in Fig. 1.1.

Initially, formation of Fe^{III} oxides predominantly involves aerobic weathering of magmatic rocks (mainly on the earth's surface) in both terrestrial and marine environments; redistribution processes between the various global compartments may follow. Such processes may involve mechanical transport by wind/water erosion from the pedosphere into the hydrosphere or atmosphere, or, more importantly, reductive dissolution followed by migration of Fe^{II} and oxidative reprecipitation in a new compartment. Iron ore formation and iron oxide precipitation in biota are important examples of redistribution. Man participates in these processes not only as a living organism, but also as a consumer of iron metal and Fe oxides for various industrial purposes. The overall result of all these processes is a continuous net increase in Fe oxides in the global system at the expense of iron in magmatic ("primary") rocks.

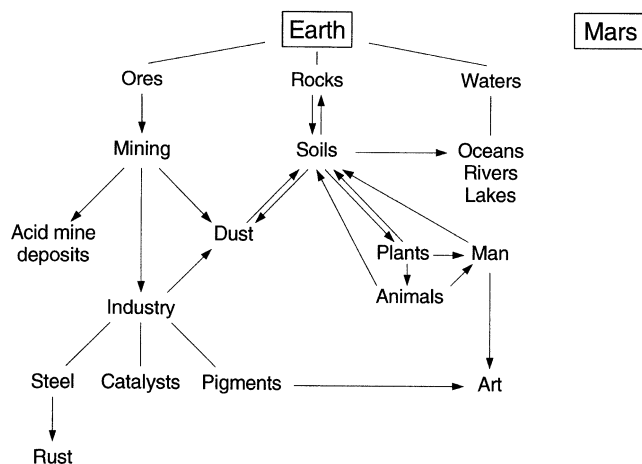


Fig. 1.1 Iron oxides in the global system

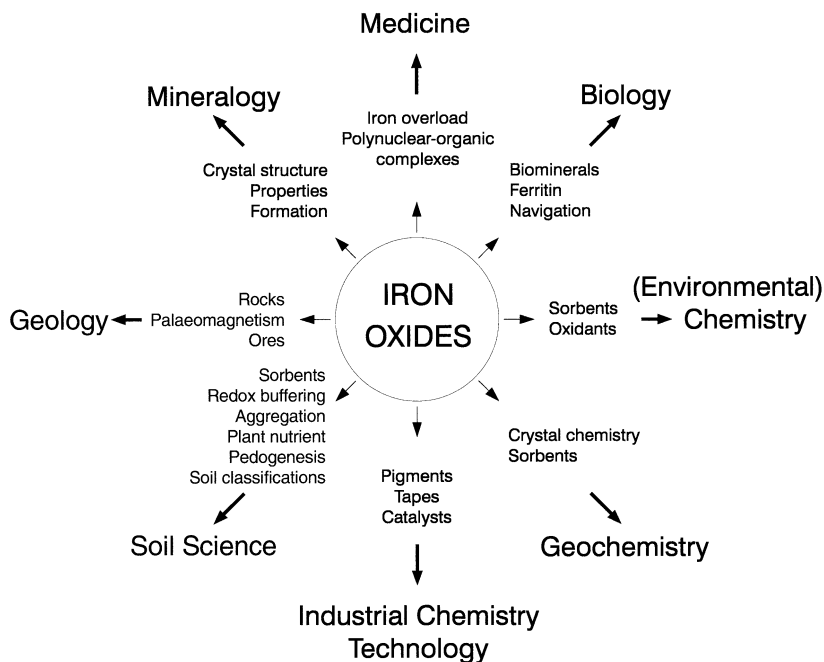


Fig. 1.2 The multidisciplinary nature of iron oxide research

The logical consequence of this widespread distribution of Fe oxides is that many different scientific disciplines (Fig. 1.2) have an interest in Fe oxides. Naturally this has led to much fruitful, interdisciplinary communication and interaction from which this book has greatly profited.

There are 16 iron oxides (Tab. 1.1). These compounds are either oxides, hydroxides or oxide-hydroxides, collectively referred to in this book as iron oxides. The iron oxides are composed of Fe together with O and/or OH. In most compounds iron is in

Tab. 1.1 The iron oxides

<i>Oxide-hydroxides and hydroxides</i>	<i>Oxides</i>
Goethite α -FeOOH	Hematite α -Fe ₂ O ₃
Lepidocrocite γ -FeOOH	Magnetite Fe ₃ O ₄ (Fe ^{II} Fe ^{III} O ₄)
Akaganéite β -FeOOH	Maghemite γ -Fe ₂ O ₃
Schwertmannite Fe ₁₆ O ₁₆ (OH) _y (SO ₄) _z · n H ₂ O	β -Fe ₂ O ₃
δ -FeOOH	ε -Fe ₂ O ₃
Feroxyhyte δ' -FeOOH	Wüstite FeO
High pressure FeOOH	
Ferrihydrite Fe ₅ HO ₈ · 4 H ₂ O	
Bernalite Fe(OH) ₃	
Fe(OH) ₂	
Green Rusts Fe ^{III} _x Fe ^{II} _y (OH) _{3x+2y-z} (A ⁻) _z ; A ⁻ = Cl ⁻ ; 1/2 SO ₄ ²⁻	

the trivalent state; three compounds – FeO , $\text{Fe}(\text{OH})_2$ and Fe_3O_4 contain Fe^{II} . Iron oxides consist of close packed arrays of anions (usually in hexagonal (hcp) or cubic close packing (ccp)) in which the interstices are partly filled with divalent or trivalent Fe predominately in octahedral (VI) – $\text{Fe}(\text{O},\text{OH})_6$ – but in some cases- in tetrahedral (IV) – FeO_4 – coordination. The various oxides differ in the way in which the basic structural units – $\text{Fe}(\text{O},\text{OH})_6$ or $\text{Fe}(\text{O})_4$ – are arranged in space. In some cases, small amounts of anions (Cl^- , SO_4^{2-} , CO_3^{2-}) may also participate in the structure. There are five polymorphs of FeOOH and four of Fe_2O_3 .

The oxide hydroxides can be dehydroxylated to their oxide counterparts. In part, this arises from the similarity between the anion frameworks which ensures that rearrangement of the cations and loss of OH are often all that is required to effect a transformation. Other characteristics of these compounds include the low solubility (= high stability) of the Fe^{III} oxides, the brilliant colours, partial replacement of Fe in the structure by other cations, in particular, Al and the catalytic activity. Owing to their high energy of crystallization, Fe oxides very often form only minute crystals both in natural environments and when produced industrially. They have, therefore, a high specific surface area, often $>100 \text{ m}^2 \text{ g}^{-1}$. This makes them effective sorbents for a large range of dissolved ions and molecules and gases. Selected properties of the iron oxides are summarized in Tables 1.2 and 1.3.

The individual oxides are described briefly below.

Goethite, $\alpha\text{-FeOOH}$, occurs in rocks and throughout the various compartments of the global ecosystem. It has the diaspore structure which is based on hexagonal close packing of anions (hcp). Goethite is one of the thermodynamically most stable iron oxides at ambient temperature and is, therefore, either the first oxide to form or the end member of many transformations. In massive crystal aggregates goethite is dark brown or black, whereas the powder is yellow and responsible for the colour of many rocks, soils and ochre deposits. Industrially goethite is an important pigment. Goethite was named in 1815 after *Johann Wolfgang von Goethe* (Fig. 1.3), 1749–1832,

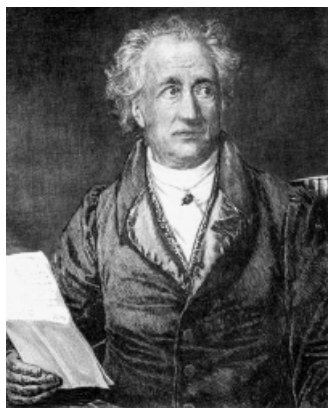


Fig. 1.3 Johann Wolfgang von Goethe (1749–1832)

Tab. 1.2 General properties of the iron oxides

<i>Mineral name</i>	<i>Goethite</i>	<i>Lepidocrocite</i>	<i>Akaganéite</i>	<i>Schwertmannite</i>	<i>Feroxyhyte</i>
	orthorhombic	orthorhombic	monoclinic	tetragonal	hexagonal
Cell dimensions (nm)	$a = 0.9956$ $b = 0.30215$ $c = 0.4608$	$a = 0.307$ $b = 1.253$ $c = 0.388$	$a = 1.0546$ $b = 0.3031$ $c = 1.0483$ $\beta = 90.63^\circ$	$a = 1.065$ $c = 0.604$	$a = 0.293$ $c = 0.456$
Formula units, per unit cell, Z	4	4	8	2	2
Density (g cm^{-3})	4.26	4.09		≈ 3.8	4.20
Octahedral occupancy	$1/2$	$1/2$	$1/2$	$1/2$	$1/2$
Colour	yellow-brown	orange	yellow-brown	orange-brown	red-brown
Hardness	5–5 $1/2$	5	–		–
Type of magnetism	antiferromag.	antiferromag.	(antiferromag.)	(antiferromag.)	ferrimag.
Néel (Curie) temperature (K)	400	77	290	–	440–460
Standard free energy of formation ΔG_f^0 (kJ mol^{-1})	–488.6	–477.7	n.k.		n.k.
Solubility product ($\text{pFe} + 3 \text{ pOH}$)	40–44	~ 42	34.8^3		n.k.

n.k. = not known; **1**) blocking temperature; **2**) Curie temperature; **3**) $\text{pFe} + 2.7 \text{ pOH}$; **4**) $\log(\text{Fe}^{2+})^3/(\text{H})^8 \cdot (\text{e})^2$

Tab. 1.3 Melting point, boiling point, heat of fusion, decomposition and vaporization of Fe oxides (Samsonov, 1982)

<i>Oxide</i>	<i>Melting point</i> $^\circ\text{C}$	<i>Boiling point</i> $^\circ\text{C}$	<i>Heat of fusion</i>	<i>Heat of decomposition</i> kJ mol^{-1}	<i>Heat of vaporization</i>
Hematite	1350 (1562) ^a	–	–	461.4	–
Magnetite	1583–1597	2623	138.16	605.0	298 at 2623 $^\circ\text{C}$
Maghemite	–	–	–	457.6	–
Wüstite	1377	2512	31.4 (for $\text{Fe}_{0.97}\text{O}$)	529.6	230.3 at 2517 $^\circ\text{C}$ (for $\text{Fe}_{0.97}\text{O}$)

Tab. 1.2 (continued)

<i>Ferrihydrite</i>	<i>Bernalite</i>	<i>Hematite</i>	<i>Magnetite</i>	<i>Maghemite</i>	<i>Wüstite</i>
hexagonal	Orthorhombic	rhombohedral hexagonal	cubic	cubic or tetragonal	cubic
$a = 0.2955$ $c = 0.937$	$a = 0.7544(2)$ $b = 0.7560(4)$ $c = 0.7558(2)$	$a = 0.50356(1)$ $c = 1.37489(7)$	$a = 0.8396$	$a = 0.83474$	$a = 0.4302-0.4275$
4	8	6	8	8	4
3.96	3.32	5.26	5.18	4.87	5.9–5.99
$<2/3$	$1/2$	$2/3$	–	–	–
red-brown	dark green	red	black	reddish-brown	black
–		$6\frac{1}{2}$	$5\frac{1}{2}$	5	5
speromag.		weakly ferromag. or antiferromag.	ferrimag.	ferrimag.	antiferromag.
25–115 ¹⁾		(956) ²⁾	(850) ²⁾	(820–986) ²⁾	203–211
–699		–742.7	–1012.6	–711.1	–251
38.0–39.5		42.2–43.3	35.7 ⁴⁾	40.4	n.k.

the famous German poet who was also a scientist and as such held the position of minister for mines for the Duke of Weimar. His mineral collection can still be visited in his house in Weimar.

The orange coloured *lepidocrocite*, γ -FeOOH, is named after its platy crystal shape (lepidos=scale) and its orange colour (krokus = saffron). It occurs in rocks, soils, biota and rust and is often an oxidation product of Fe^{2+} . It has the boehmite (γ -AlOOH) structure which is based on cubic close packing (ccp) of anions.

Akaganéite, β -FeOOH, is named after the Akagané mine in Japan where it was first discovered (Mackay, 1962). It occurs rarely in nature and is found mainly in Cl-rich environments such as hot brines and in rust in marine environments. Unlike the other FeOOH polymorphs, it has a structure based on body centered cubic packing of anions (bcp) (hollandite structure) and contains a low level of either chloride or fluoride ions. It has a brown to bright yellow colour.

Schwertmannite, $\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n\text{H}_2\text{O}$, has the same basic structure as akaganéite, but contains sulphate instead of chloride ions. This recently recognized mineral frequently occurs in nature as an oxidation product of pyrite and can be

easily synthesized (Bigham et al. 1994). The y/z ratio appears to vary. Whereas Bigham et al. (1990) noticed a range of 3.3-6 for natural samples, Yu et al. (2002) found synthetic samples to be higher in sulphate and possibly even free from OH.

δ -FeOOH (synthetic) and its poorly crystalline mineral form, ferroxhyte (δ -FeOOH), are reddish-brown, ferrimagnetic compounds. Their structures are based on hcp anion arrays and differ in the ordering of the cations. Ferroxhyte was first described by Chukhrov et al. in 1976 and occurs (rarely) in various surface environments.

In contrast, the reddish-brown *ferrihydrite* (often wrongly termed “amorphous iron oxide” or “hydrous ferric oxide (HFO)”) is widespread in surface environments. It was first described by Chukhrov et al. in 1973. Unlike the other iron oxides it exists exclusively as nano-crystals and unless stabilized in some way, transforms with time into the more stable iron oxides. Ferrihydrite is, thus, an important precursor of more stable and better crystalline Fe oxides. Structurally ferrihydrite consists of hcp anions and is a mixture of defect-free, and defective structural units. The composition, especially with respect to OH and H₂O, seems to be variable. A preliminary formula, often used, is Fe₅O₈H · H₂O.

Another recently identified mineral is *bernalite*, Fe(OH)₃, a greenish hydroxide that to date has only been found in two locations (Birch et al. 1993; Kolitsch, 1998).

Fe(OH)₂ does not exist as a mineral. The Fe is divalent and the structure which is based on a hcp anion array, is similar to that of brucite. Pure Fe(OH)₂ is white. It is, however, readily oxidized, upon which it develops into greenish-blue, so-called, green rust or, on further oxidation, into black magnetite.

Hematite, α -Fe₂O₃, is the oldest known Fe oxide mineral and is widespread in rocks and soils. Its colour is blood-red (Greek haima = blood) if finely divided and black or a sparkling grey if coarsely crystalline. Hematite has the corundum (α -Al₂O₃) structure which is based on a hcp anion packing. Like goethite, it is extremely stable and is often the end member of transformations of other iron oxides. Hematite is an important pigment and a valuable ore; it is a major constituent of the so-called, banded iron formations. Other names for hematite include iron^{III} oxide, ferric oxide, iron sesquioxide, red ochre, specularite, specular iron ore, kidney ore, crocus martis and martite.

Magnetite, Fe₃O₄, is a black, ferrimagnetic mineral containing both Fe^{II} and Fe^{III}. It has an inverse spinel structure. Magnetite is an important iron ore. Together with titanomagnetite, it is responsible for the magnetic properties of rocks; these are the object of palaeomagnetic studies. It is formed in various organisms in which it serves as an orientation aid. Other names for magnetite include black iron oxide, magnetic iron ore, iron^{II,III} oxide, loadstone* (when natural polarity is present), tri-iron tetroxide, ferrous ferrite, Hercules stone and Magneteisenerz (German). Some of these names are in current use, although they are not recognized as mineral names. They reflect the diversity of disciplines for which this mineral is of interest.

Maghemite, γ -Fe₂O₃, is a red-brown, ferrimagnetic mineral isostructural with magnetite, but with cation deficient sites. It occurs in soils as a weathering product of

* Magnetite is attracted by a magnet but ordinarily, it cannot, itself, attract iron particles.

magnetite or as the product of heating of other Fe oxides, usually in the presence of organic matter. Maghemite is an important magnetic material. A fascinating account of the laboratory history of maghemite is given by Dronskovsky (2001).

$\beta\text{-Fe}_2\text{O}_3$ (Braun & Gallagher, 1972) and $\varepsilon\text{-Fe}_2\text{O}_3$ are rare compounds that have been synthesized only in the laboratory. The former has been obtained by dehydroxylation of $\beta\text{-FeOOH}$ under high vacuum at 170°C . $\varepsilon\text{-Fe}_2\text{O}_3$ was first reported in 1934 (Forestier & Guillot-Guillain) and named in 1963 (Schrader & Buttner). It exists both as a disordered, pure form and an ordered form which appears to be associated with hematite or maghemite. Its structure is intermediate between those of hematite and maghemite. It can be prepared in various ways and transforms to hematite at between 500 and 750°C , apparently according to the method of preparation.

High-pressure FeOOH is another rare, laboratory compound that has been prepared by hydrothermal conversion of hematite in NaOH at 400°C and pressures of 8 GPa (Pernet et al. 1973).

Wüstite, FeO , is the other iron oxide which contains only divalent Fe. It is usually non-stoichiometric (O-deficient). The structure is similar to that of NaCl and is based on ccp anion packing. Wüstite is black. It is an important intermediate in the reduction of iron ores.

Green Rusts are a group of Fe oxides consisting of layers of $\text{Fe}^{\text{II}}\text{OH}$ octahedra in which some Fe^{II} is replaced by Fe^{III} and, to maintain neutrality, anions, especially Cl^- and SO_4^{2-} are bound between the layers. Green rusts are formed as corrosion products (hence the name).

2

Crystal structure

2.1

General

Almost all the iron oxides, hydroxides and oxide hydroxides are crystalline. The degree of structural order and the crystal size are, however, variable and depend on the conditions under which the crystals were formed. All Fe oxides display a range of crystallinities except for ferrihydrite and schwertmannite which are poorly crystalline.

Certain iron oxides are isostructural with other metal oxides. Goethite, for example, is isostructural with diaspore (α - AlOOH) and hence, is sometimes referred to as having the diaspore structure. Iron oxides and their isostructural metal oxides are listed in Table 2.1.

2.2

Iron oxide structures

The structures of iron oxides have been determined principally by single crystal X-ray diffraction or neutron diffraction with supplementary information coming from infrared spectroscopy, electron diffraction and high resolution electron microscopy. A few years after the first successful application of X-ray diffraction to crystal structure determination, this technique was used to establish the major features of the structures of magnetite (Bragg, 1915; Nishikawa, 1915) and hematite (Bragg & Bragg, 1918).

Table 2.2 summarizes basic crystallographic data for the iron oxides. Iron oxides, hydroxides and oxide hydroxides consist of arrays of Fe ions and O^{2-} or OH^- ions. As the anions are much larger than the cations (the radius of the O^{2-} ion is 0.14 nm, whereas those of Fe^{III} and Fe^{II} are 0.065 and 0.082 nm, respectively), the arrangement of anions governs the crystal structure and the ease of topological interconversion between different iron oxides. Table 2.3 lists the atomic coordinates of the iron oxides.

There are two basic ways of representing the crystal structures of iron oxides – either in terms of the anion arrangement (packing) or as linkages of octahedra and/

Tab. 2.1 Structural types of the iron oxides

<i>Structural type</i>	<i>Fe oxide</i>	<i>Isostructural compounds</i>
Diaspore	Goethite	Diaspore (α -AlOOH) Groutite (α -MnOOH) Ramsdellite (α -MnO ₂) Montroseite (VOOH) Bracewellite (α -CrOOH) ScOOH, GaOOH
Boehmite	Lepidocrocite	Boehmite (γ -AlOOH)
Hollandite	Akaganéite	Hollandite (BaMn ₈ O ₁₆)
	Schwertmannite	Cryptomelane (KMn ₈ O ₁₆)
Corundum	Hematite	Corundum (α -Al ₂ O ₃) Ilmenite (FeTiO ₃)
	Bernalite	Perovskite (CaTiO ₃)
Brucite	Fe(OH) ₂	Brucite (Mg(OH) ₂) Ni(OH) ₂ , Ca(OH) ₂ , β -Co(OH) ₂
Inverse spinel	Magnetite	Jacobsite (Fe ^{III} Mn ^{II} Fe ^{III} O ₄) Magnesioferrite (FeMgFeO ₄) Ulvospinel (Fe ₂ TiO ₄)
Defect spinel	Maghemite	
InOOH	high pressure FeOOH	InOOH, CrOOH, GaOOH, RhOOH, ScOOH
Defect NaCl	FeO ϵ -Fe ₂ O ₃	Manganosite (MnO) GaFeO ₃ , AlFeO ₃

or tetrahedra formed from a central cation and its nearest anion neighbours (ligands). The polyhedra models shown in the figures of this section were produced by H. Stanjek¹⁾ using the program ATOMS (Dowty, 1991).

2.2.1

Close packing of anion layers

Iron oxides are made up of close packed arrays of anions. The commonest arrangements of these sheets of anions in the third dimension are hexagonal close packing (hcp), where the sheets are stacked ABAB ..., and cubic close packing (ccp) with ABCABC ... stacking. Only akaganéite, with a body-centred cubic (bcc) anion arrangement, lies somewhat outside this scheme. The sheets of anions are stacked along some particular crystallographic direction with an average distance between anion layers of 0.23–0.25 nm for all iron oxides.

There are twice as many interstices between the sheets of anions as there are anions in a layer. The cations fit into the octahedral (sixfold coordination) or the smaller, tetrahedral interstices. For compounds with Fe^{III} ions, charge balance require-

¹⁾ Lehrstuhl für Bodenkunde, Technische Universität München, 85350 Freising-Weihenstephan, Germany

Tab. 2.2 Crystallographic data for iron oxides

Compound	Crystallographic system	Space group	Stacking of close packed anions	Unit cell dimensions nm				Z
				a	b	c	β°	
Goethite*	Orthorhombic	Pnma	ABAB [001]	0.9956	0.30215	0.4608		4
Lepidocrocite*	Orthorhombic	Bbmm	ABCABC [015]	0.3071	1.2520	0.3873		4
Akaganéite	Monoclinic	I2/m	bcc	1.056	0.3031	1.0483	90.63	8
Schwertmannite	Tetragonal	P4/m		1.066		0.604		
Feroxyhyte	Hexagonal	P3ml	ABAB [001]	0.293		0.456		2
δ -FeOOH	Hexagonal	P3ml	ABAB [001]	0.293		0.449		1
HP FeOOH	Orthorhombic	Pn2 ₁ m		0.4932	0.4432	0.2994		2
Ferrihydrite	Hexagonal	P31 c; P3	ABAB [001]	0.2955		0.937		4
Hematite	Hexagonal (Rhombohedral)	R $\bar{3}$ c	ABAB [001]	0.5034		1.3752		6
Magnetite	Cubic	Fd3m	ABCABC [111]	0.8396				8
Maghemite	Cubic	P4 ₃ 32	ABCABC [111]	0.83474				8
	Tetragonal	P4 ₁ 2 ₁ 2		0.8347		2.501		24
Wüstite	Cubic	Fm3m		0.4302 (high Fe)				
				0.4275 (low Fe)				
ϵ -Fe ₂ O ₃	Orthorhombic	Pna2 ₁		0.5095	0.879	0.9437		8
Fe(OH) ₂	Hexagonal	P3ml		0.3262		0.4596		1
Bernalite	Orthorhombic	Immm		0.7544	0.7560	0.7558		8

* Goethite and lepidocrocite have recently been moved from Pbnm to Pnma and from Cmcmm to Bbmm, respectively. As a result of this change, the crystal planes and directions in this book are different from those in the 1st edition.

ments ensure that only a proportion of the interstices can be filled and this opens up the possibility of several different arrangements of cations between the anion sheets. Differences between the iron oxide structures arise as a result of variations in the arrangements of cations in the interstices and, to a lesser extent, differences in the stacking of the sheets of anions. The anion sheets are held together by the cations and/or by hydrogen bonds.

The goethite, hematite and Fe(OH)₂ structures are all based on hcp anion stacking with different ordered arrangements of the cations. The unit cells of goethite and hematite are related to the simple hexagonal unit cell of Fe(OH)₂ and can be regarded as superlattices produced by ordering the cations in different ways in the oxygen framework. The common anion framework permits topological changes to take place relatively easily. During dehydroxylation of goethite to hematite, for example, pairs of water molecules along the *a*-axis of the goethite crystal are removed while the anion array remains intact.

The cations in these compounds are Fe^{III} and/or Fe^{II}. In iron oxides, Fe^{III} is always in the high spin (unpaired d electrons) state. As Fe^{III} with five d electrons has no crystal field stabilization energy (CFSE; see Chap. 6), regardless of whether it is octahedrally or tetrahedrally coordinated, there is little preference for one or the other type of site. For Fe^{II}, on the other hand, CFSE is higher for octahedral than for tetrahedral coordination, so the octahedral coordination is favoured.

Tab. 2.3 Atomic coordinates of the iron oxides

Oxide		Atomic coordinates			Ref.
		x	y	z	
Goethite	Fe	0.145	1/4	−0.045	1
	O ₁	−0.199	1/4	0.288	
	O ₂	−0.053	1/4	−0.198	
	H	−0.08	1/4	−0.38	
Lepidocrocite	Fe	0	−0.3137	1/4	2
	O ₁	0	0.2842	1/4	
	O ₂	0	0.0724	1/4	
	H	0	0.514	0.366	
Akaganéite	Fe ₁	0.858	0	0.341	3
	Fe ₂	0.339	0	0.141	
	O ₁	0.663	0	0.290	
	O ₂	0.657	0	0.030	
	O ₃	0.293	0	0.357	
	O ₄	0.039	0	0.332	
	Cl	0	0	0	
Feroxyhyte	Fe ₁	0	0	0	4
	Fe ₂	0	0	1/4	
	O	1/3	2/3	0.246	
	H	1/3	2/3	0.510	
Hematite	Fe	0	0	0.3553	5
	O	0.3059	0	1/4	
Ferrihydrite, 6-line Defect-free phase	Fe	1/3	2/3	0.136	6
	O,OH ₁	0	0	0	
	O,OH ₂	2/3	1/3	1/4	
	Fe ₁	1/3	2/3	0.163	
	Fe ₂	1/3	2/3	0.337	
	Fe ₃	1/3	2/3	0.663	
	Fe ₄	1/3	2/3	0.837	
	O,OH ₁	0	0	0	
	O,OH ₂	2/3	2/3	1/2	
Magnetite	Fe ₁	1/8	1/8	1/8	7
	Fe ₂	1/2	1/2	1/2	
	O	0.25468	0.25468	0.25468	
Maghemite <i>P4₃32</i>	Fe ₁	0.9921	0.9921	0.9921	8
	Fe ₂	0.8650	0.6150	7/8	
	Fe ₃	3/8	1/8	7/8	
	O ₁	0.861	0.861	0.861	
	O ₂	0.372	0.377	0.876	
Maghemite <i>P4₁2₁2</i>	Fe ₁	0.7421	0.9921	0.03903	8
	Fe ₂	0.2579	0.0079	0.2057	
	Fe ₃	0.4921	0.7579	0.1224	
	Fe ₄	0.6150	0.6150	0	
	Fe ₅	0.385	0.385	1/6	
	Fe ₆	3/8	0.135	0.08	

Tab. 2.3 (continued)

Oxide		Atomic coordinates			Ref.
		x	y	z	
Maghemite $P4_12_12$	Fe ₇	0.865	5/8	0.0867	
	Fe ₈	7/8	0.365	0.003	
	Fe ₉	1/8	1/8	0	
	O ₁	0.611	0.861	-0.0047	
	O ₂	0.361	0.889	0.0787	
	O ₃	0.389	0.139	0.162	
	O ₄	0.122	0.377	0.0003	
	O ₅	0.877	0.378	0.0837	
	O ₆	0.878	0.623	1/6	
	O ₇	0.374	0.628	0.0007	
	O ₈	0.128	0.126	0.084	
	O ₉	0.626	0.372	0.1673	
	O ₁₀	0.373	0.376	0.0843	
Wüstite	O ₁₁	0.624	0.627	0.0843	9
	O ₁₂	0.124	0.873	0.001	
	Fe	0	0	0	
	O	1/2	1/2	1/2	

1) Szytula (1968), 2) Christensen & Norlund-Christensen (1978), 3) Post and Buchwald (1991), 4) Patrat et al., (1983), 5) Fleet (1984), 6) Jansen et al. (2002), 7) Blake et al. (1966), 8) Shmakov et al. (1995), 9) Fakisika (1967)

In ideally close packed anion arrays, the O-O distance is 0.304 nm for octahedrally coordinated Fe^{II}, whereas for Fe^{III} it is 0.29 nm in octahedral and 0.33 nm in tetrahedral coordination. In fact, the anion packing for most Fe oxides is not entirely regular because the cations are slightly larger than the interstices. In Figure 2.1, the interlayer (in the *c*-direction) versus intralayer spacings are plotted for the various iron oxides. The points for magnetite and maghemite fall on the straight line indicating that anion packing in these oxides is regular; for goethite, hematite, δ -FeOOH and Fe(OH)₂, however, the anion packing is slightly distorted (Mackay, 1961).

2.2.2

Linkages of octahedra or tetrahedra

The basic structural unit in these compounds is the Fe(O)₆ or FeO₃(OH)₃ octahedron, or more rarely, the Fe(O)₄ tetrahedron. These entities may be linked by corners, edges or faces (Fig. 2.2) or by combinations of these linkages to form different structural arrays (Fig. 2.3). The Fe-Fe distances depend on the type of linkage and for octahedra are longest for corner-sharing and shortest for face-sharing arrangements (Tab. 2.4). The linkage representation is useful for visualizing the different structures and their relationships to each other (Fig. 2.3).

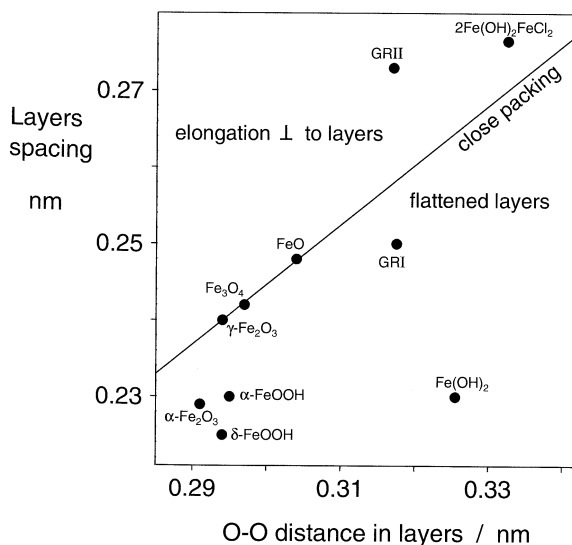


Fig. 2.1 Relationship between the inter-layer spacing and the intra-layer spacing (O–O distance) in the hexagonal close packed and cubic close packed iron oxide structures (Mackay, 1961, with permission). GR I, GR II: Green rust I and II

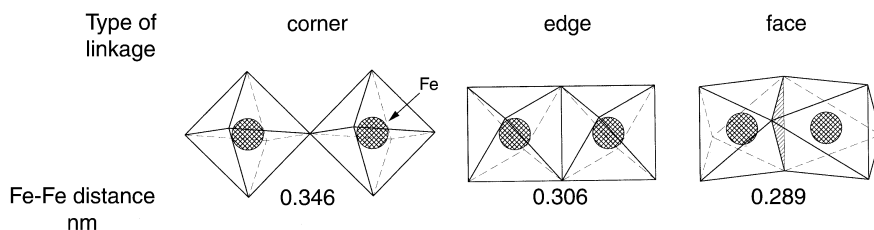


Fig. 2.2 Different linkages of octahedra in Fe^{III} oxides and their Fe-Fe distances (data from Manceau & Combes, 1988).

2.3

Structures of the individual iron oxides

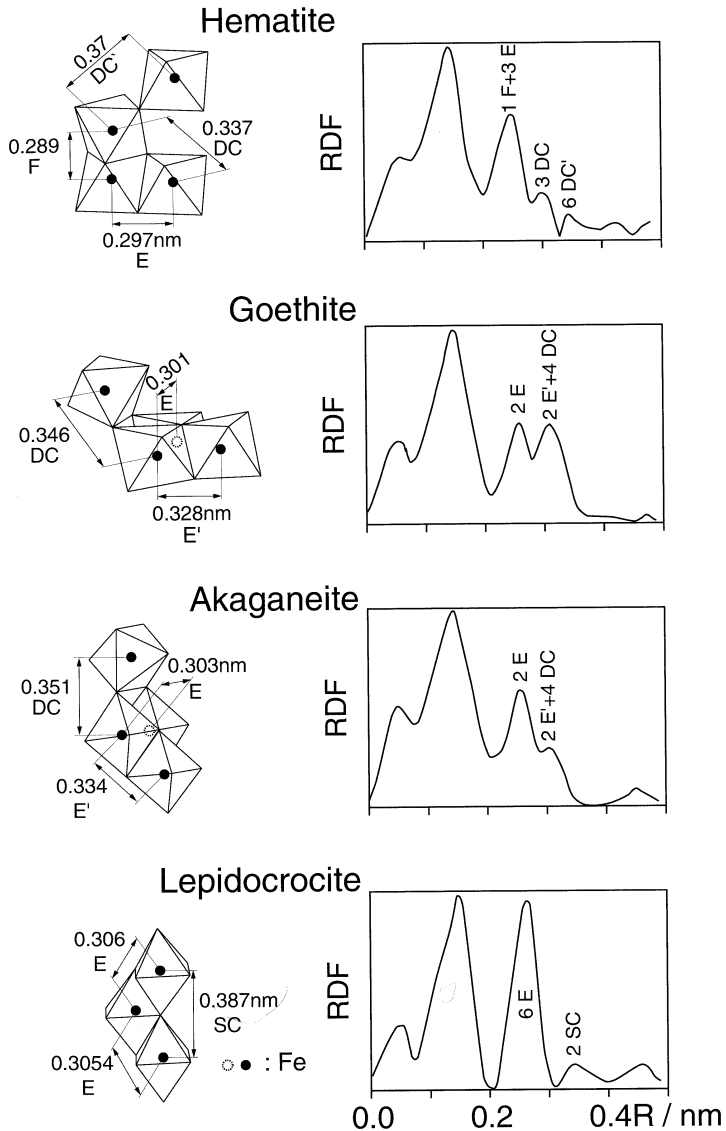
2.3.1

The oxide hydroxides

The building unit common to all five oxide hydroxides (α ; β ; γ ; δ ; high pressure) is the $\text{FeO}_3(\text{OH})_3$ octahedron, spatially arranged in five different ways.

2.3.1.1 Goethite α -FeOOH

Goethite (named after J.W. von Goethe) is isostructural with diaspore and with various other metal oxides (Tab. 2.1). It has an orthorhombic unit cell with $a = 0.9956$ nm, $b = 0.30215$ nm, $c = 0.4608$ nm (Goldsztaub, 1932; Hoppe, 1941; Forsyth



C, C': corner E, E': edge F : face contact

S : single D : double

RDF : radial distribution function

Fig. 2.3 Basic structural units and Fe-Fe distances (in nm) for hematite, goethite, akaganéite and lepidocrocite and their associated radial distribution functions as obtained from EXAFS spectra. The first peak in the radial distribution

function corresponds to the oxygen shell surrounding the Fe atom and the second and third peaks to nearest and next-to-nearest Fe neighbours (Manceau & Drits, 1993, with permission).

Tab. 2.4 Dependence of Fe-Fe distances in iron oxide hydroxide on type of octahedral linkage (Adapted from Manceau & Combes, 1988; with permission)

Compound	Face shared	Fe-Fe distances (nm) for		Ref.
		Edge shared octahedra	Corner shared octahedra	
Goethite	–	0.301		
		0.328	0.346	1
Lepidocrocite	–	0.306	0.371	2
Akaganéite	–	0.304	0.366	3
Feroxyhyte	0.288	0.295–0.318	0.339	4
Hematite	0.289	0.297	0.370	
			0.339	5

1) Szytula et al. (1968), 2) Oles et al. (1970), 3) Szytula et al. (1970), 4) Patrat et al. (1983),

5) Blake et al. (1966)

et al., 1968; Szytula et al., 1968; Sampson, 1969)¹⁾. In addition to mirror planes, the unit cell contains glide planes *a* (glide component $a/2$) and *n* (component $(b + c)/2$). The unit cell edge lengths are slightly different for most metal substituted goethites (see Chap. 3). In addition, the *c* edge length is sensitive to disorder in the crystal and, as disorder increases, may increase from 0.460 nm to 0.463 nm (Schulze, 1984; Schwertmann et al., 1985; Schwertmann & Carlson, 1994). There are four formula units per unit cell.

The goethite structure consists of an hcp array of anions (O^{2-} and OH^-) stacked along the [010] direction with Fe^{III} ions occupying half the octahedral interstices within a layer (Fig. 2.4a–c). The Fe ions are arranged in double rows separated by double rows of empty sites (Fig. 2.4a,c); at the crystal surfaces the empty sites appear as grooves (Fig. 2.4d).

Each Fe ion is surrounded by three O^{2-} and three OH^- to give $FeO_3(OH)_3$ octahedra and the structure is usually described in terms of these octahedra. Double chains of octahedra formed by edge sharing run parallel to the [100] direction (Fig. 2.4d). These chains are linked to adjacent double chains by corner-sharing with one chain being displaced by $b/2$ with respect to its neighbours. This arrangement of the double chains ultimately leads to the orthorhombic symmetry. The structure, therefore, consists of double chains of octahedra alternating with double chains of vacant sites; although the latter appear as “tunnels” in the model in Figure 2.4d, it can be seen from the close packed anion arrangement (Fig. 2.4a) that they are not true tunnels. Figure 2.4f shows the atomic arrangement in the {011} plane commonly displayed in real goethite crystals (see Chap. 4).

The goethite structure contains two types of O atoms designated as O_I and O_{II} (Fig. 2.4e). On the O_I site, the O atom is shared between octahedra of two different double chains, whereas the O_{II} atom is shared between octahedra in the same chain and is also linked to the proton. Neutron scattering has shown that the $O_{II}-O_{II}$ distance is

1) The space group was changed from Pbnm to Pnma leading to $a \rightarrow c$; $b \rightarrow a$ and $c \rightarrow b$.

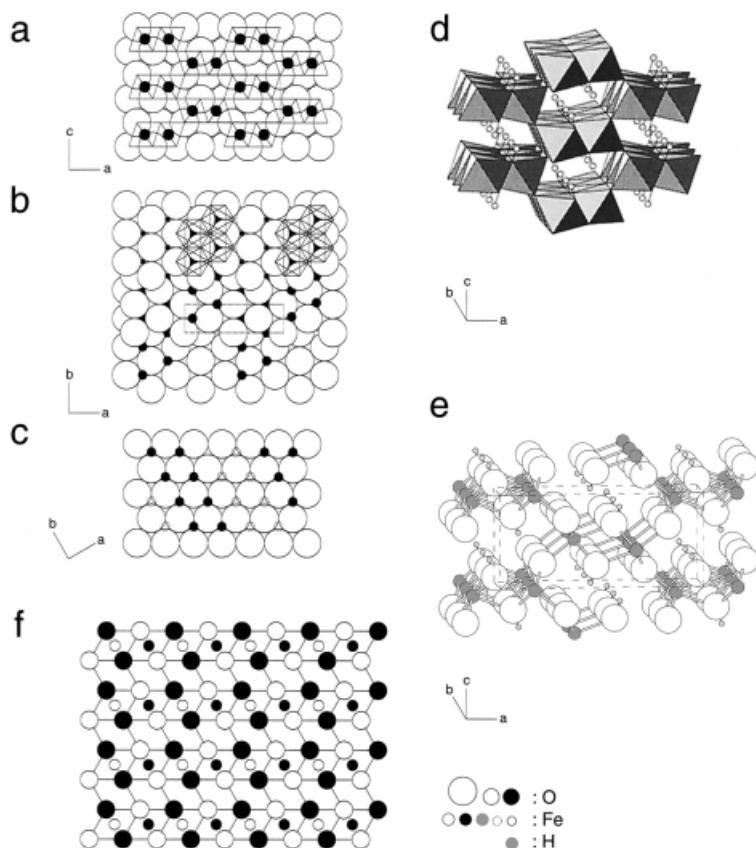


Fig. 2.4 Structure of goethite. a) Hexagonal close packed anion arrangement and distribution of cations in the octahedral interstices; projection on (010) with the cation pairs indicated and the unit cell outlined. b) Projection on (001) with the unit cell and the octahedral arrangement indicated. c) Projection down [001]. Dashed circles represent Fe in the next lower layer. d) Arrangement of octahedral double chains. H atoms also shown. e) Ball-and-stick model with unit cell out-

lined. H atoms also shown. I and II refers to O atoms shared between octahedra of two different double chains and between octahedra of the same chain, respectively. f) Projection of the atomic structure on (001). Black and open circles indicate anions at different elevations. (a, b: Eggleton et al., 1988; with permission; c: Waychunas, 1991; with permission; d, e: Stanjek, unpubl.; f: Misawa et al., 1974; with permission)

shorter than that of other O–O distances in the structure. As a result, the double chains of octahedra are twisted slightly with respect to each other (Fig. 2.4d, e). Each Fe in an octahedron is surrounded by four nearest Fe atoms across edges (${}^4\text{E}$) and four next to nearest Fe neighbours across corners (${}^4\text{C}$) (cf Fig. 11.3).

Non-linear hydrogen bonds pass diagonally across the empty cation sites in the goethite structure. These bonds help link the chains of octahedra; the hydrogen bond joins an O_{II} of one octahedron to an O_{I} of an octahedron in a chain diagonally

opposite. The H atom does not lie on the O_I-O_{II} vector, but makes an angle of 11.6° with it. As the H atom is located closer to the O_{II} atom, the whole entity can be considered to be an OH group. The O–H...O distance is 0.276 nm and the O_{II} –H distance is 0.099 nm. All the hydrogen bonds are structurally equivalent, but point in two different directions.

XRD patterns of synthetic goethite frequently show selective line broadening. One cause of this effect can be small crystallite size; another, in larger crystals, is internal disorder. Although HRTEM has shown that goethite is crystallographically, extremely homogeneous (Cornell et al., 1983; Mann et al., 1985), there is indirect evidence, mainly from DTA studies (Schulze, 1984; Schwertmann, 1984; Schwertmann et al., 1985), IR and magnetic measurements (van Oosterhout, 1964; Schwertmann et al., 1985) for some kind of internal disorder in goethite. One such piece of evidence is the variation of the unit cell edge length c . Goethites synthesized in alkaline solution at temperatures of $4\text{--}40^\circ\text{C}$ had a significantly higher value of c (0.462 nm), and presumably more internal defects than goethite synthesized at temperatures of $50\text{--}90^\circ\text{C}$ ($c = 0.461$ nm) (Schwertmann et al., 1985). It has been suggested that a form of internal disorder may exist particularly in the [001] direction. Bonding is weakest along the [001] direction because the hydrogen bonding between the double chains of octahedra has its strongest vector in this direction. Regular spaces around one nm across have been observed in HRTEM micrographs of ultra-thin sections of crystals taken perpendicular to [010] (Smith & Eggleton, 1983; Schwertmann, 1984a; Van der Woude et al., 1984). On heating to 230°C , the c -value can be reduced (Fey & Dixon, 1981; Schwertmann & Carlson, 1994). The same effect was obtained by improving crystallinity through constant stirring of the ferrihydrite suspension ($0.3\text{ M [OH]}; 70^\circ\text{C}$) during its transformation to goethite: the crystals became larger (MCLc:11 $\rightarrow$ 21 nm), c (but not a and b) decreased significantly from 0.4620(1) to 0.4611(2) nm and the difference between the two OH-bending modes at ca. 900 and 800 cm^{-1} was reduced from 99 to 95 cm^{-1} . It thus appears that stirring during crystal growth reduces the number of crystal defects and/or Fe-vacant sites in the structure (Schwertmann & Stanjek, 1998). The vacant sites are compensated for by extra, non-stoichiometric H^+ which, as shown by Yapp and Poths (1995), is isotopically exchangeable at RT whereas the stoichiometric H^+ is not. The amount of non-stoichiometric H^+ in natural goethite could be as much as 20% of the total OH.

2.3.1.2 Lepidocrocite $\gamma\text{-FeO(OH)}$

Lepidocrocite (Greek: *lepidos* = scale, flake and *krokoeis* = saffron-coloured) is isostructural with boehmite (Tab. 2.1). Unlike goethite and akaganéite which have a tunnel structure, lepidocrocite is a layered compound. The orthorhombic unit cell contains four formula units and has the edge lengths, $a = 1.2520(6)$ nm; $b = 0.3873(2)$ nm and $c = 0.3071(6)$ nm (Ewing, 1935; Oles et al., 1970; Christensen & Nørlund-Christensen, 1978).

The structure consists of arrays of ccp anions (O^{2-}/OH^-) stacked along the [150] direction with Fe^{III} ions occupying the octahedral interstices (Fasiska, 1967) (Fig. 2.5a-c). The [150] direction of the orthorhombic unit cell corresponds to the

[111] direction of a distorted cubic cell and this relationship facilitates dehydroxylation to a spinel phase. Figure 2.5 f shows the atomic arrangement of the {110} plane.

Like goethite and akaganéite, lepidocrocite consists of double chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedra running parallel to the c -axis. The double chains share edges with adjacent double chains and each chain is displaced by half, with respect to its neighbour, thus forming corrugated sheets of octahedra (Fig. 2.5 d). These sheets are stacked perpendicular to the [100] direction and are separated by double rows of empty octahedral sites. The sheets are held together solely by hydrogen bonds (Fig. 2.5 d, e). Deuteration of the bulk OH in lepidocrocite is facilitated by the layer structure: ease of deuteration of FeOOH follows the order lepidocrocite $\gg$ goethite $>$ akaganéite (Ishikawa et al., 1986).

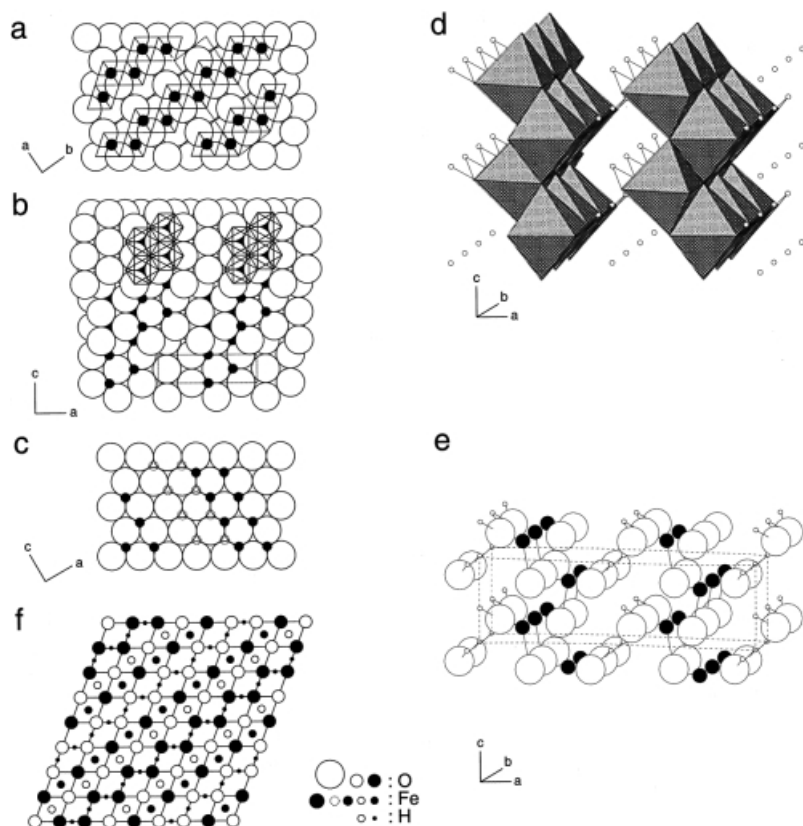


Fig. 2.5 Structure of lepidocrocite. a) Cubic close packed anion arrangement and distribution of cations over the octahedral interstices. Projection on (001). Octahedral arrangement and unit cell outlined. b) Projection of anion close packing on (010). Octahedral arrangement and unit cell outlined. c) Projection of anion close packing on (001). Dashed circles represent Fe in the next lower layer. d) Arrangement of oc-

tahedral double chains in corrugated layers. H-bonds between layers also shown. e) Ball-and-stick model with unit cell outlined. H-bonds also shown. f) Atomic structure projected on (110). (a, b: Eggleton et al., 1988; with permission; c: Waychunas, 1991; with permission; d, e: Stanjek, unpubl.; f: Misawa et al., 1974; with permission)

The proton lies on the vector joining two O_{II} atoms (Fig. 2.5 e). Neutron diffraction studies (Christensen & Nørlund-Christensen, 1978) suggest that the proton is closer to one oxygen than to the other; the $OH\cdots O$ bond length of 0.268 nm is made up of 0.093 nm ($O-H$) and 0.175 nm ($H\cdots O$).

2.3.1.3 Akaganéite $\beta\text{-FeO(OH)}$ and schwertmannite $\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n \text{H}_2\text{O}$

Akaganéite (named after the Akagané mine in Japan) is isostructural with hollandite. Compounds with this structure have a tetragonal or monoclinic unit cell. Bernal et al. (1959) and Keller (1970) both concluded that the unit cell of akaganéite was tetragonal with $a = 1.000$ nm and $c = 0.3023$ nm. The structural refinement of a natural sample using XRD and Rietveld analysis indicated, however, that the unit cell is monoclinic with $a = 1.060$ nm, $b = 0.3039$ nm, $c = 1.0513$ nm and $\beta = 90.24^\circ$ (Post & Buchwald, 1991). There are eight formula units per unit cell.

Akaganéite differs from all other iron oxides and hydroxides in that the anions are arranged in a *body-centred* cubic array (instead of hcp or ccp). For this reason akaganéite is less dense than α - and $\gamma\text{-FeOOH}$. The Fe^{III} ions are on the octahedral sites. The structure consists of double chains of edge-shared octahedra running parallel to the fourfold symmetrical b -axis (Fig. 2.6a). The double chains share corners with adjacent chains to give a three-dimensional structure containing tunnels bounded by double rows of octahedra and with a cross section of 0.5 nm^2 . There is one tunnel per unit cell (Fig. 2.6b). These are true tunnels in which a single row of anions is missing. The tunnels run parallel to the b -axis and are delineated by (110) planes.

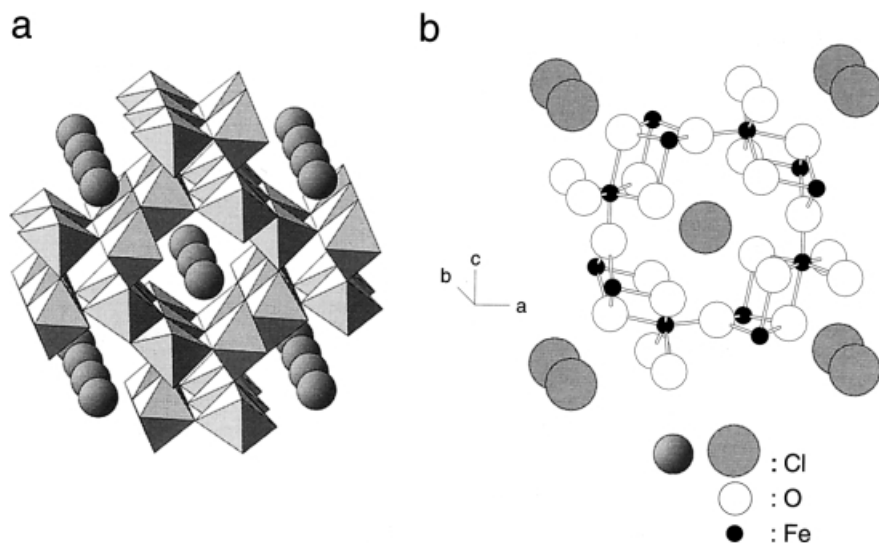


Fig. 2.6 Structure of akaganéite. a) Arrangement of octahedral double chains in tunnels with chloride ions in the centre of the tunnels. b) Ball-and-stick model with unit cell outlined. (a, b: Stanjek, unpubl.)

Early investigations appeared to indicate that akaganéite had a substructure (Watson et al., 1962). Each crystal was considered to consist of bundles of rods, 5 unit cells across with each rod containing a tunnel with an internal diameter of 3.0 nm, i.e. hollow subcrystals. This structure was later questioned when reversible N_2 adsorption/desorption isotherms were obtained (Paterson & Tait, 1977). Eventually the matter was resolved when electron microscopic examination of ultrathin sections of akaganéite crystals showed that true 3.0 nm pores were absent (some pores developed due to heating in the TEM beam) and in addition, HRTEM indicated that akaganéite is crystallographically homogeneous (Galbraith et al., 1979), i.e. the proposed substructure was shown to be an artefact. TEM features such as mottling and the development of striations, which had appeared to provide support for a substructure, arose from radiation damage in the electron beam. Subsequently, Maeda and Hachisu (1983) examined Schiller layers of akaganéite in the SEM and noted a number of 3.0 nm pores. These pores were external features, however, and arose quite naturally from the packing together of round needles of akaganéite.

Both Mössbauer data and XRD results have shown that there are two types of octahedra and hence, Fe sites in the structure (Johnson & Logan, 1979; Murad, 1979; Post & Buchwald, 1991). In one type of octahedron, the Fe-O distances range from 0.19 and 0.23 nm, whereas in the second type, they are between 0.18 and 0.23 nm. Both types of octahedra are slightly distorted, probably as a result of cation/cation repulsion between adjacent octahedra.

Hydrogen bonding in the akaganéite structure appears to be weak. The shortest hydrogen bond length (0.285 nm) is longer than that in ice and water suggesting that the OH groups are nearly free (Gallagher & Phillips, 1969). The OH bond length is 0.93–1.01 nm and the OH vectors are directed towards the centres of the tunnels (Post & Buchwald, 1991). The open tunnel is ca. 0.21–0.24 nm across. The activation energy of 97 J mol⁻¹ for tritium exchange in akaganéite is well above that for goethite (34.3 J mol⁻¹) and lepidocrocite (58.7 J mol⁻¹) (Gallagher & Phillips, 1969).

The tunnels in the akaganéite structure are considered to be stabilized by Cl⁻ ions (Fig. 2.6a, b). Levels of Cl⁻ ranging from 2 to 7 mol % have been reported; the average is 1.23 Cl⁻ ions per unit cell and this corresponds to an average occupancy of two thirds of the tunnels. The extent of incorporation of Cl⁻ appears to be related to the concentration of the starting FeCl₃ solution from which the akaganéite is produced, being higher for a 0.1 than a 0.06 M solution (Chambaere & DeGrave, 1984). A portion of chloride ions can be washed out of the crystals, but a minimum amount of 0.25–0.5 mmol mol⁻¹ appears to be essential to stabilize the structure (Ellis et al., 1976). Complete removal of the chloride ions leads to transformation to goethite or hematite depending on the pH. Some authors have reported that akaganéite contains water, but infrared evidence (Keller, 1970) and XRD data (Post & Buchwald, 1991) suggest that the amount of water in the tunnels is negligible. In contrast to the above, Naono et al. (1993) found the proposed model with Cl⁻ located in the center of the tunnel inconsistent with the high amount (as compared to goethite and lepidocrocite) of water vapour adsorption. They proposed that the Cl⁻ ion instead belongs to the ligand shell of the Fe together with O²⁻ and OH⁻ and that the tunnel

takes up the H_2O molecules. Some support comes from agreement between the available tunnel space ($17 \text{ mm}^3 \text{ g}^{-1}$) with that measured with adsorbed H_2O ($16.3 \text{ mm}^3 \text{ g}^{-1}$).

Other ions besides Cl^- can be accommodated in the akaganéite tunnels. The F^- ion, but not the larger Br^- ion, can replace Cl^- , and other ions which are smaller than 0.35 nm in diameter (e.g. OH^-) may also be present. Up to $70 \text{ g kg}^{-1} \text{ F}$ is reported to be present in akaganéite (Chambaere & De Grave, 1984). Naono et al. (1993) have produced an F-akaganéite with the composition $\text{FeO}(\text{OH})_{0.7}\text{F}_{0.3} \cdot 0.3 \text{ H}_2\text{O}$. Sulphate may also occupy the tunnel of the akaganéite structure, but in this case an entirely new mineral, *schwertmannite* (named after U. Schwertmann), is formed (Bigham et al., 1990; 1994). Its general, simplified formula is $\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_z \cdot n \text{ H}_2\text{O}$ where $16 - y = 2z$ and $2.0 \leq z \leq 3.5$. The mineral has a primitive, tetragonal cell with $a = 1.066$ and $c = 0.604 \text{ nm}$. The probable space group is P4/m . In contrast to the halogenides, the oxyanions are considered to share oxygen atoms with Fe^{III} of the tunnel wall thereby leading to some distortion of the structure. As a consequence of this, the XRD lines of schwertmannite are considerably broadened and some lines of akaganéite, for example, the $hk0$ lines including the strongest 110 line at 0.74 nm , are totally absent (see Chap. 7). This indicates reduced crystal development in the direction perpendicular to the tunnel direction $[110]$; only very thin needles a few nm wide can be observed (see Chap. 4). A mineral of similar composition was described by Glocker as long ago as in 1853 and 1858 and was named after him in 1855 by Naumann. The name was discredited, however, in 1977 (Nickel & Mandarino, 1977) after Fojt (1975) suggested that the compound was identical to lepidocrocite.

In addition to sulphate, selenate (J. M. Bigham, unpubl.) and chromate (S. Regenspurg; unpubl.) can also be incorporated in the tunnels of synthetic schwertmannite. Whether or not two different Se-O distances (based on EXAFS) attributable to surface and tunnel selenate, respectively, exist in the Se-form is still under discussion (Waychunas et al., 1995, 1995a). The Cr form has the bulk composition $\text{Fe}_{16}\text{O}_{16}(\text{OH})_{10.23}(\text{CrO}_4)_{2.88}$. In fact, synthetic schwertmannite formed in the sulphate/arsenate system tolerates arsenate only up to a $\text{As}/(\text{As}+\text{S})$ mole ratio of ca. 0.5, and it is likely that most of this arsenate is surface-bound. Above this ratio, a new, very poorly ordered Fe-hydroxy arsenate with two broad XRD peaks at ca. 0.31 and 0.16 nm and B_{hfs} at 4.2 K and ca. 1.5 K of 41.6 and 47.3 T , respectively, forms (Carlson et al. 2002). From this one may conclude that, whereas the tetrahedral oxyanions with hexavalent central cations (S; Se; Cr) can be accommodated in the tunnel positions, the pentavalent cations can not, or not as easily. Schwertmannite from acid mine water contained between 6 and $70 \text{ g kg}^{-1} \text{ As}$ (Carlson et al. 2002).

2.3.1.4 $\delta\text{-FeOOH}$ and $\delta'\text{-FeOOH}$ (feroxyhyte)

$\delta\text{-FeOOH}$ is isostructural with $\text{Fe}(\text{OH})_2$. It has a hexagonal unit cell with $a = 0.294 \text{ nm}$ and $c = 0.449 \text{ nm}$. A related compound exists in nature under the mineral name feroxyhyte (named by F.V. Chukhrov; see Chukhrov et al., 1976), also termed $\delta'\text{-FeOOH}$. Feroxyhyte has a hexagonal unit cell with $a = 0.294 \text{ nm}$ and $c = 0.456 \text{ nm}$. It contains two formula units per unit cell, whereas the unit cell of the synthetic material contains only one formula unit.

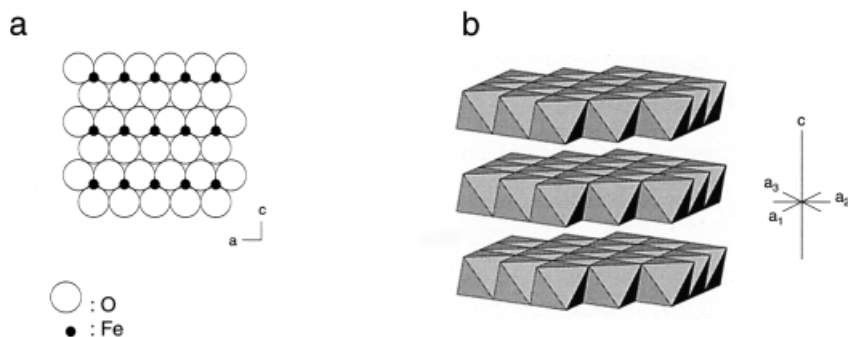


Fig. 2.7 Structure of feroxyhyte. a) Hexagonal close packed anion layer with cations distributed over the interstices. b) Layers of edge-sharing octahedra. (a, b: Stanjek, unpubl.)

The structure of δ -FeOOH is based on a disordered hcp array of anions with Fe^{III} ions distributed over half the octahedral sites in an ordered manner (Fig. 2.7 a). The sequence along the [001] direction is that of two filled sites followed by two vacant sites (Patrat et al., 1983). The structure can also be represented as sheets of edge-sharing octahedra (Fig. 2.7 b). There is some evidence that around $1/5$ of the cation sites may be tetrahedral. The packing of anions in this synthetic material is disordered. The Fe arrangement found by Patrat et al. (1983) is supported by the XRD simulation work of Drits et al. (1993 a) who also suggested that there is some octahedral face-sharing, 5% stacking faults and some displacement of Fe away from the centre of the octahedra. The nearest Fe-Fe distances were calculated to be 0.288, 0.339 and 0.373 nm in good agreement with those found from EXAFS (Manceau & Drits, 1993).

The natural and synthetic compounds differ in the arrangement of cations; in both compounds the anion packing is disordered. Feroxyhyte is a disordered form of the synthetic material with the cations being distributed almost entirely randomly over the interstices.

2.3.1.5 High pressure FeOOH

The unit cell of this modification of FeOOH is orthorhombic with $a = 0.4932$ nm, $b = 0.4432$ nm and $c = 0.2994$ nm. It can be prepared by heating α - Fe_2O_3 in NaOH at 500°C and 8 MPa for one hour (Chenavas et al., 1973). There are two formula units per unit cell. The structure resembles that of deformed TiO_2 . It consists of single chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedra linked by edges and running along the c -axis. Each chain is linked to its neighbour by corner sharing (Fig. 2.8 a, b).

2.3.1.6 Ferrihydrite

Both synthetic and natural ferrihydrite (named by F.V. Chukhrov; see Chukhrov et al., 1973) are poorly ordered. The degree of ordering is variable and a range of XRD

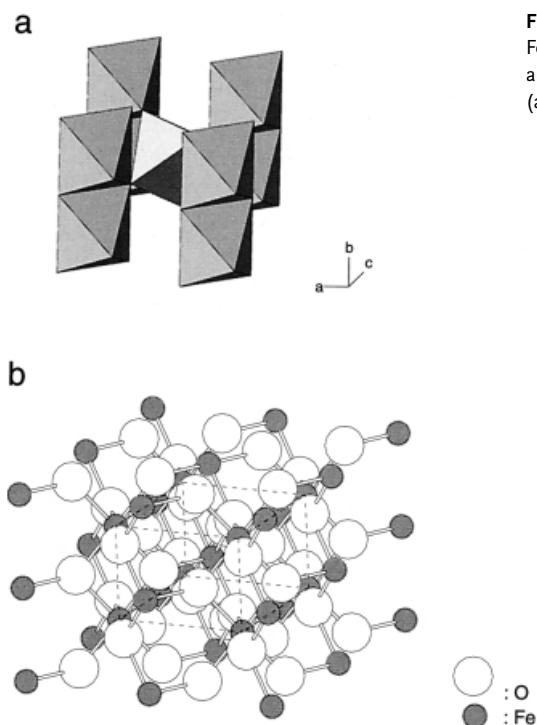


Fig. 2.8 Structure of high pressure FeOOH. a) Octahedral chains. b) Ball-and-stick model with unit cell outlined. (a, b: Stanjek, unpubl.)

patterns may be obtained. The two extremes of crystal order are referred to as 2-line and 6-line ferrihydrite because the XRD patterns show 2 or 6–8 reflections as structural order increases (see Fig. 7.16). Ferrihydrites with intermediate crystallinity form as the reaction conditions are varied systematically. For example, the crystallinity falls, i.e. the number of X-ray peaks decreases from 6–8 to 2, as the rate of Fe^{III} hydrolysis increases (Lewis, 1992, Schwertmann & Cornell, 2000) or, alternatively, if oxidation of Fe^{2+} at pH 7 is hindered by the presence of increasing concentrations of such interfering compounds as silicate (Schwertmann et al. 2000) and soil organic matter (Schwertmann et al. unpubl.). Once formed, ferrihydrite does not become more crystalline with time.

The structure of ferrihydrite has been the object of numerous studies in the past and several different structures have been proposed. The main difficulty affecting elucidation of the structure is the low degree of order. The original models of Towe and Bradley (1967) and Chukhrov et al. (1976) are based on XRD data and involve a defective hematite structure based on an hcp array of anions with vacant Fe^{III} sites and a considerable amount of water. The Fe^{III} ions are distributed randomly over the interstices and there is more OH^- and H_2O and less Fe^{III} in ferrihydrite than in hematite, i.e. there is a lower Fe/O ratio ($<2/3$).

The unit cell parameters given by Towe and Bradley (1967) for 6-line ferrihydrite are $a = 0.508 \text{ nm}$ and $c = 0.94 \text{ nm}$. There are four formula units per unit cell. A con-

sequence of the random distribution of cations is that the two strong 012 and 104 XRD reflections of hematite at 0.367 nm and 0.269 nm, which are derived from the ordering of Fe, are missing in ferrihydrite; the strong asymmetry of the 0.25 nm reflection on the low-angle side of the peak may, however, be assigned to incipient ordering of Fe. Furthermore, the repeat unit of stacking in the anionic array is four instead of six as in hematite.

Further refinements of the structure are based on the agreement between experimental and simulated XRD data (Drits et al., 1993;1995) in combination with structural data from EXAFS spectra (Manceau & Drits, 1993). According to these results, 6-line ferrihydrite contains three intergrown structural components (Fig. 2.9, upper):

- (1) defect-free consisting of ABACA.....anion close packing with the Fe atoms only at octahedral sites and with 50% occupancy; the unit cell is hexagonal with $a = 0.296$ nm and $c = 0.949$ nm and a space group P-31c;
- (2) defective with ABA and ACA structural fragments occurring with equal probability in a random sequence and with the Fe atoms within each fragment being identically ordered in a hexagonal super-cell with $a = 0.5126$ nm, space group P3, and
- (3) ca. 25% as ultradispersed 1–2 nm hematite.

The main difference between 6- and 2-line ferrihydrite is in the size of their crystal domains.

The structure derived from a Rietveld fit of a neutron diffraction pattern of a 6-line ferrihydrite which showed more and sharper lines (Fig. 2.9, lower) than an XRD pattern, was in agreement with the structure proposed by Drits et al. (1993) except that it was not necessary to assume the presence of hematite in order to produce a satisfactory fit (Jansen et al. 2002). The unit cell of the defect free phase had $a = 0.29514(9)$ nm and $c = 0.9414(9)$ nm and the average domain size derived from line broadening was 2.7(0.8) nm. Since forced hydrolysis of an Fe^{III} solution at elevated temperatures will ultimately lead to hematite, it is likely that incipient hematite formation may occur under certain synthesis conditions. Neither these studies nor Mössbauer spectroscopy, which showed only a singular isomer shift at 4.2 K characteristic of $^{\text{VI}}\text{Fe}$, supported the presence of $^{\text{IV}}\text{Fe}$ (Cardile, 1988; Pankhurst & Pollard, 1992). However, the presence, at the surface, of some Fe with lower (<6) coordination, perhaps as tetrahedra (Eggleton and Fitzpatrick, 1988) which may have become unsaturated on heating, has been suggested on the basis of XAFS results (Zhao et al. 1994).

Structural order in both 2-line (1–3nm) and 6-line ferrihydrite is also clearly visible in HRTEM images which show lattice fringes throughout (see Fig. 4.18) (Janney et al. 2000a). Selected area electron nano-diffraction (SAED; <1nm) patterns of a 2-line ferrihydrite showed diffuse streaks rather than distinct reflections (Janney et al. 2000). Two bright rings at ~0.15 and 0.25 nm and numerous faint rings suggest that 2-line ferrihydrite has a two-dimensional structure consisting of a basic tetrameric unit, as proposed by Feitknecht et al. (1973), with disordered stacking of close-packed anion layers and randomly distributed Fe atoms. Hexagonal stacking of double chains of face-sharing octahedra is likely. The SAED pattern of the 5–6 nm particles of 6-line ferrihydrite showed lattice fringes spaced between 0.25 and 0.148 nm

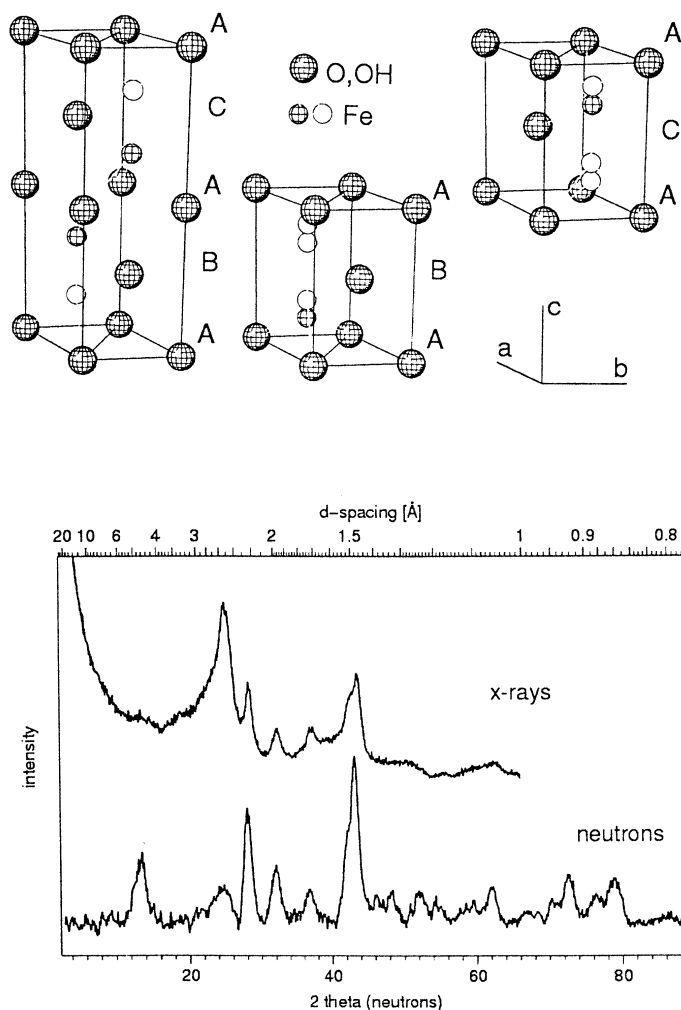


Fig. 2.9 Upper: Model of the two structural components of ferrihydrite. *Left*: defect-free ABACA phase; *Right*: two defective ABA and ACA phases. Open circles represent vacant Fe sites. Lower: Comparison of a neutron with an X-ray diffractogram of 6-line ferrihydrite (Jansen et al. 2002, with permission)

in agreement with XRD, as well as seven additional fringes with spacings of between 0.135 and 0.086 nm.

An exact formula for ferrihydrite has yet to be established because a precise separation of structural OH and H₂O from adsorbed water has not been successful to date. Towe & Bradley (1967) originally suggested the bulk formula Fe₅HO₈ · 4H₂O which is certainly to be preferred over Fe(OH)₃. Infrared measurements using D₂O exchange have suggested that ferrihydrite contains OH⁻ and O²⁻

with around half the protons being present as OH^- and the remainder as water (150 g/kg) (Russell, 1979). Stanjek and Weidler (1992) found that heating at 127 °C for ca. 1000 hr lowered the $\text{H}_2\text{O}/\text{Fe}_2\text{O}_3$ ratio from 2.64 to 1.23 for 2-line ferrihydrite and from 1.57 to 0.85 mol mol⁻¹ for 6-line ferrihydrite without noticeable modification of the X-ray diffractogram, i.e. with hardly any transformation to hematite. Assuming that all the remaining weight loss was due to OH, the bulk composition (per 3 O) of the 6-line ferrihydrite was then $\text{Fe}_{1.55}\text{O}_{1.66}(\text{OH})_{1.34}$ and that of 2-line ferrihydrite was $\text{Fe}_{1.42}\text{O}_{1.26}(\text{OH})_{1.74}$. Electron Energy Loss spectra (EELS) of two biotically formed 2-line ferrihydrites gave Fe/O ratios after freeze-drying of 0.50(6) (Mavrocordatos & Fortin, 2001). In view of these results, a formula with less OH/ H_2O than those of Towe & Bradley (1967) [$\text{Fe}_{1.33}\text{O}(\text{OH})_2$] and Chukhrov et al. (1973) [$\text{Fe}_{1.42}\text{O}_{1.26}(\text{OH})_{1.74}$] appears closer to the real composition of 6-line ferrihydrite. In fact, the OH/Fe ratio is probably somewhere between the two extremes, i.e. $0.15 < \text{OH}/\text{Fe} < 3$ with a mol ratio of 0.86 rather than 3, being suggested as being closer to a structure with octahedral face-sharing and Fe-deficient sites (Stanjek & Weidler, 1992).

2.3.2

The Hydroxides

2.3.2.1 Bernalite $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$

A new Fe^{III} oxide, bernalite (named after J.D. Bernal), was accepted as a mineral in 1992 (Birch et al., 1992, 1993). Its empirical formula is $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$. Powder X-ray diffraction suggested a cubic structure with $a = 0.7568$ nm, isostructural with perovskite (CaTiO_3) and consisting of four corner-sharing octahedra per unit cell (Fig. 2.10a), but single crystal studies indicated an orthorhombic cell with $a = 0.7544$, $b = 0.7560$ and $c = 0.7558$ nm. Water molecules are considered to occupy a fraction of the large 8-coordinated positions in the structure (Fig. 2.10b). The number of formula units per unit cell is eight. The name bernalite was given to crystals discovered in museum samples taken from the Broken Hill mine (NSW, Australia) around the beginning of the century. A second occurrence of bernalite from the Clara Mine in the Black Forest (Germany) was characterized by Walenta (1995; 2001).

2.3.2.2 $\text{Fe}(\text{OH})_2$

This compound is isostructural with brucite ($\text{Mg}(\text{OH})_2$) and CdI_2 . The unit cell is hexagonal with $a = 0.3258$ nm and $c = 0.4605$ nm. The structure consists of sheets of corner-sharing, trigonally distorted $\text{Fe}(\text{OH})_6$ octahedra stacked along the [001] direction. The Fe^{II} ions occupy only half the available octahedral interstices and this results in a structure in which each filled layer of sites alternates with an empty layer of sites. The OH radical behaves as a single entity. Amakinite is a rare mineral of the composition $(\text{Fe}, \text{Mg}, \text{Mn})(\text{OH})_2$, also with brucite structure. $\text{Fe}(\text{OH})_2$ is readily oxidized by air and even by water, upon which the colour changes from white to brownish. The structure can be maintained up to a replacement of one tenth Fe^{II} by Fe^{III} (Bernal et al., 1959).

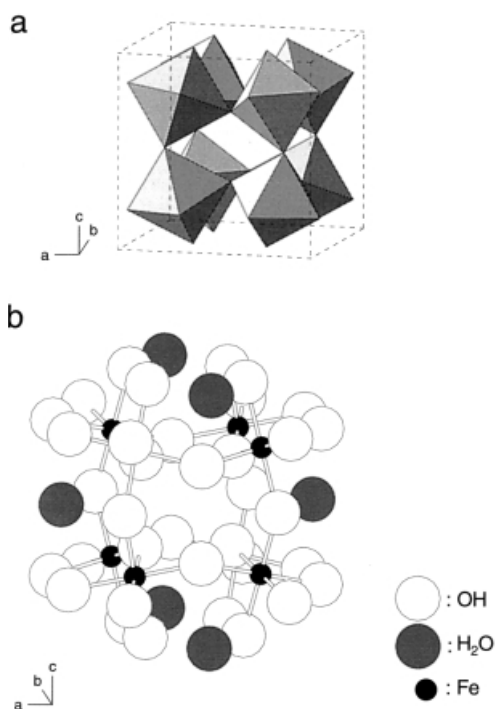


Fig. 2.10 Structure of bernalite. a) Octahedral model with unit cell outlined. b) Ball-and-stick model (Stanjek, unpubl.)

2.3.2.3 Green rusts

Green rusts are a group of blueish-green $\text{Fe}^{\text{II}} - \text{Fe}^{\text{III}}$ hydroxy compounds which are formed under anoxic conditions during the corrosion of steel and are also found in anoxic soils (Trolard et al. 1997). They are isostructural with pyroaurite, $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3$ and consist of sheets of hcp $\text{Fe}^{\text{II}}(\text{OH})_6$ octahedra ($\text{Fe}(\text{OH})_2$ structure) in which some of the Fe^{II} is replaced by Fe^{III} : the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio is between 0.8 and 3.6. The Fe^{III} creates a positive layer charge which is balanced by anions located between the sheets of octahedra (Feitknecht & Keller, 1950; Bernal et al., 1959; Stampfl, 1969; Brindley & Bish, 1976; Taylor & McKenzie, 1980; Refait et al. 1997). Of the anions, chloride (green rust I) and sulphate (green rust II) are the best known. In addition to these, the other halogenides, carbonate, perchlorate and nitrate (Lewis, 1997; Tab. 2.5) as well as oxalate (Refait et al. 1998) and selenate (Refait et al. 2000) can also be placed between the layers. The parameters of the rhombohedral unit cell of green rust I are $a = 0.3198 \text{ nm}$ and $c = 2.42 \text{ nm}$ and the hexagonal unit cell of green rust II has $a = 0.317$ and $c = 1.09 \text{ nm}$. In the nitrate, sulphate and chlorate forms, a layer of water molecules is intercalated; this layer can be removed by evacuation, as shown by the reduction of d_{001} by about 0.25 nm , which corresponds to the diameter of a water molecule. As seen from the d-values in Table 2.5, the interlayer spacings increase with the size of the halogenide anions: Cl^- : 0.181 ; Br^- : 0.196 ; I^- : 0.220 nm . Since none of the anions in Table 2.5 could be detected in the green rust found in a soil, it is assumed that OH^- is the interlayer anion and a

Tab. 2.5 X-ray data for Green Rusts containing different interlayer anions (data from Lewis, 1997; with permission)

Anion	Cl^-	Br^-	I^-	CO_3^{2-}	NO_3^-	SO_4^{2-}	ClO_4^-
				Hydrated			
d_{003}/nm	0.795	0.806	0.838	0.753	—	—	—
d_{001}/nm	—	—	—	—	1.097	1.119	1.102
				Evacuated			
d_{003}/nm	0.774	0.779	0.802	0.750	—	—	—
d_{001}/nm	—	—	—	—	0.742	0.828	0.837

composition of between $Fe_2^{II}Fe^{III}(OH)_7$ and $Fe^{II}Fe_2^{III}(OH)_7$ has been suggested (Trolard et al. 1997).

2.3.3

The Oxides

2.3.3.1 Hematite α - Fe_2O_3

Hematite (Greek: haima = blood) is isostructural with corundum. The unit cell is hexagonal with $a = 0.5034$ nm and $c = 1.375$ nm (Bragg & Bragg, 1918; Pauling & Hendricks, 1925; Blake et al. 1966; Sata & Akimoto, 1979). There are six formula units per unit cell. For hexagonal symmetry, the Miller indices are (hkil); i may be replaced by a dot or omitted (as in this book) as $h + k = -i$. Hematite may also be indexed in the rhombohedral system. For the rhombohedral unit cell, $a_{rh} = 0.5427$ nm and $\alpha = 55.3^\circ$ and there are two formula units per cell.

The structure of hematite can be described as consisting of hcp arrays of oxygen ions stacked along the [001] direction, i.e. planes of anions are parallel to the (001) plane (Fig. 2.11 a). Two thirds of the sites are filled with Fe^{III} ions which are arranged regularly with two filled sites being followed by one vacant site in the (001) plane thereby forming sixfold rings (Fig. 2.11 b).

The arrangement of cations produces pairs of $Fe(O)_6$ octahedra. Each octahedron shares edges with three neighbouring octahedra in the same plane and one face with an octahedron in an adjacent plane (Fig. 2.11 c). Face-sharing occurs along the c -axis. This face-sharing of octahedra is responsible for the distortion of the cation sublattice from ideal packing; Fe atoms in the octahedra which share faces are repelled along the direction normal to the [001], causing the cations to shift closer to the unshared faces. The O–O distances along the shared face of an octahedron are shorter (0.2669 nm) than the distance along the unshared edge (0.3035 nm), hence the octahedron is trigonally distorted (Fig. 2.11 d). The oxygen and Fe arrangement around a shared face is depicted in Figure 2.11 e; this Fe-O₃-Fe triplet structure influences the magnetic properties of the oxide.

Structural relationships exist between certain planes in the hematite structure and those in other iron oxides, namely magnetite and goethite (Tab. 2.6). There is, for example, a relationship between the (111) plane of magnetite and (001) plane of hema-

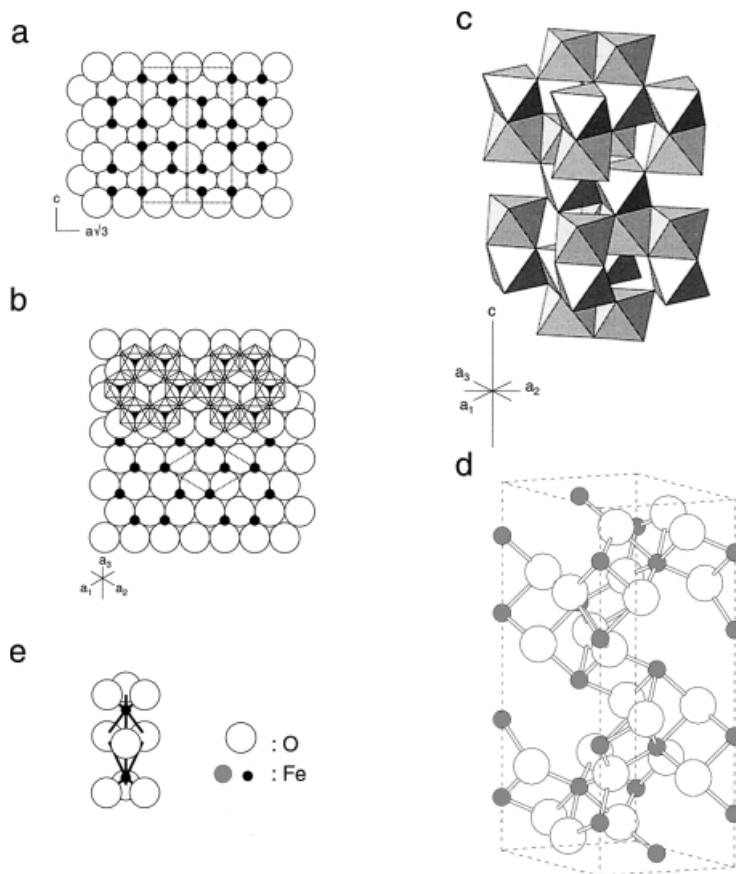


Fig. 2.11 Structure of hematite. a) Hexagonal close packing of oxygens with cations distributed in the octahedral interstices. Unit cell outlined. b) View down the c -axis showing the distribution of Fe ions over a given oxygen layer and the hexagonal arrangement of octahedra. Unit cell outlined. c) Arrangement of octahedra. Note their face-sharing. d) Ball-and-stick model. Unit cell outlined. e) $\text{O}_3\text{-Fe-O}_3\text{-Fe-O}_3$ triplets. (a, b: Eggleston et al., 1988; with permission; c, d: Stanjek, unpubl.; e: Stanjek, 1991; with permission)

Tab. 2.6 Structural orientation between iron oxides

Oxide pair	Crystal plane	Crystal direction
Goethite	(100) (004) (200)	[100]
Hematite	(003) (110) (100)	[100]
Hematite	(001)	[100]
Magnetite	(111)	[110]
Lepidocrocite	(100)	[001] [051]
Maghemite	(001)	[110] [111]

tite, hence nucleation and growth of magnetite on the (001) plane of hematite is sometimes observed. Similarly, as a result of the structural match between the (100) goethite planes and the (003) hematite planes, epitaxial growth of goethite on hematite may occur.

To provide charge balance, O^{2-} may be partly replaced by OH^- accompanied by Fe^{III} vacancies. These anion-substituted hematites are sometimes called *hydrohematite* (better: hydroxyl-hematite) or *protohematite*. The general formula is $Fe_{2-x/3}(OH)_xO_{3-x}$ (Wolska & Schwertmann, 1989). For synthetic Al-substituted hematites, the incorporation of hydroxyl groups was found to be a function of Al substitution and of synthesis temperature (Stanjek & Schwertmann, 1992). The lower the temperature, the higher is the level of anion substitution. OH^- -containing hematite can also be formed as a transition phase during the dehydroxylation of goethite. It has a defect structure and displays XRD peak broadening (Wolska & Schwertmann, 1989a). Hydroxyl groups also expand the hematite unit cell slightly and decrease the X-ray peak intensities. This allows the determination of OH^- content from the X-ray peak intensities (Stanjek & Schwertmann, 1992). As with goethite, synthesis temperature also affects the unit cell parameters of hematite; Stanjek (1991) noticed an increase in a from 0.5033 to 0.5042 nm as the synthesis temperature decreased from 100 to 25 °C. Structural disorder and incorporation of OH^- is thought to cause this effect. There was a significant correlation (<0.001 level of significance) established between the loss on ignition between 197 to 797 °C and the differences in the unit cell a , c , and V parameters for 56 different hematites (Stanjek & Schwertmann, 1992).

It has been suggested that besides OH^- , hematite synthesized at low temperatures also contains H_2O (Dang et al., 1998). The decrease in the a and c unit cell parameters between 200 and ca. 500 °C is due to the loss of OH/H_2O . Wolska & Schwertmann (1989) noticed that whereas c decreases further above 500 °C, a increases and explained this as being due to structural reorganization during the transition of goethite to hematite. The bulk formula when a is at a minimum is approximately $Fe_{1.83}O_{2.5}OH_{0.5}$. Dang et al. (1998) showed, however, that a goethite precursor is not needed for there to be an increase in a . Refinement of the XRD pattern is probably required to substantiate these conclusions. With respect to the nomenclature, both *proto-* and *hydrohematite* are used to refer to these OH/H_2O -containing hematites, but these terms may not be needed in view of the fact that minor deviations from stoichiometry are very common in oxides, especially in the nano-size range.

2.3.3.2 ϵ - Fe_2O_3

In 1963 Schrader & Büttner proposed a monoclinic unit cell for the ordered form of ϵ - Fe_2O_3 . Subsequently and on the basis of both XRD and ED data, Tronc et al. (1998) obtained an orthorhombic unit cell with $a = 0.5095$ nm, $b = 0.8789$ nm and $c = 0.9437$ nm. The space group is $Pna2_1/C_{2v}^9$. There are eight formula units per unit cell. The structure (Fig. 2.12) is described in terms of triple chains of octahedra which share edges and single chains of tetrahedra which share corners: both types of chain run parallel to the a direction. The triple chains are linked by corners and this arrangement gives rise to cavities through which pass the chains of tetrahedra. The cations are distributed over both octahedral and tetrahedral sites.

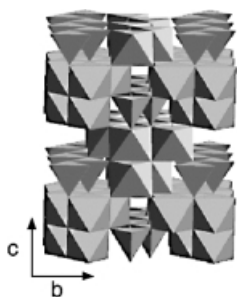


Fig. 2.12 Structure of ϵ - Fe_2O_3 (Tronc et al. 1998; with permission)

2.3.3.3 Magnetite Fe_3O_4

The main details of the structure of magnetite were established in 1915; this was one of the first mineral structures to which X-ray diffraction was applied (Bragg, 1915; Nishikawa, 1915). The structure is that of an inverse spinel (Hill et al., 1979). Magnetite has a face-centered cubic unit cell based on 32 O^{2-} ions which are regularly cubic close packed along the [111]. The unit cell edge length is $a = 0.839$ nm. There are eight formula units per unit cell.

Magnetite differs from most other iron oxides in that it contains both divalent and trivalent iron. Its formula is written as $\text{Y}[\text{XY}]_4\text{O}_4$ where $\text{X} = \text{Fe}^{\text{II}}$, $\text{Y} = \text{Fe}^{\text{III}}$ and the brackets denote octahedral sites¹⁾ (M sites). Eight tetrahedral sites (T sites) are distributed between Fe^{II} and Fe^{III} , i.e. the trivalent ions occupy both tetrahedral and octahedral sites. The structure consists of octahedral and mixed tetrahedral/octahedral layers stacked along [111] (Fig. 2.13 a). Figure 2.13 b shows the sequence of Fe- and O-layers and a section of this structure with three octahedra and two tetrahedra is depicted in Figure 2.13 c.

Magnetite is frequently non-stoichiometric in which case it has a cation deficient Fe^{III} sublattice. In stoichiometric magnetite $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}} = 0.5$. The divalent iron may also be partly or fully replaced by other divalent ions (e.g. Mn^{II} to Zn^{II}). Fitting of guest ions into the structure is assisted by the flexibility of the oxygen framework which can expand or contract to accommodate cations which differ in size from Fe^{II} . Cation substitution is accompanied by changes in the unit cell edge length (see Chap. 3).

2.3.3.4 Maghemite γ - Fe_2O_3

Maghemite (*magnetite – hematite*) has a structure similar to that of magnetite. It differs from magnetite in that all or most Fe is in the trivalent state. Cation vacancies compensate for the oxidation of Fe^{II} .

Maghemite has a cubic unit cell the a value of which was first determined by Hägg (1935). The currently accepted value of a is 0.834 nm. Each cell of maghemite contains 32 O^{2-} ions, $21\frac{1}{3}$ Fe^{III} ions and $2\frac{1}{3}$ vacancies. Eight cations occupy tetrahedral sites and the remaining cations are randomly distributed over the octahedral

1) In a normal spinel structure, the formula is XY_2O_4 with 8 M^{II} ions occupying the tetrahedral sites and 16 M^{III} ions occupying the octa-

hedral sites. Sometimes the sites occupied by Fe^{III} are termed B and those by Fe^{II} , A, i.e. $\text{B}[\text{AB}]\text{O}_4$.

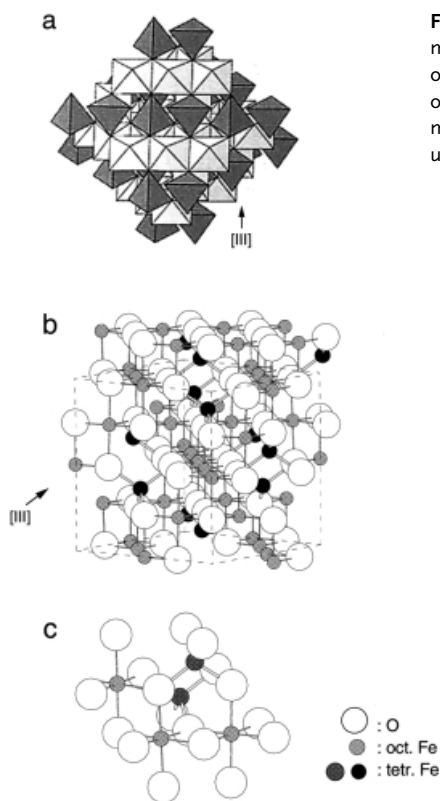


Fig. 2.13 Structure of magnetite. a) Polyhedral model with alternating octahedra and tetrahedra layers. b) Ball-and-stick model. Unit cell outlined. c) Ball-and-stick model of the arrangement of octahedra and tetrahedra. (a–c: Stanjek, unpubl.)

sites (Waychunas, 1991). The vacancies are confined to the octahedral sites. This gives the formula $^{\text{IV}}\text{Fe}_8[^{\text{VI}}\text{Fe}_{13.3}\square_{2.67}]\text{O}_{32}$ ($\square$ = vacant sites) and the space group Fd3m.

Synthetic maghemite often displays superstructure forms which arise as a result of cation and, therefore, vacancy ordering (Van Oosterhout & Rooijmans, 1958; Bernal et al. 1959). The extent of vacancy ordering is related to the crystallite size and the nature of the precursor and the amount of Fe^{II} in the structure. Feitknecht (1964) found that as synthetic crystals of Fe₃O₄ ca. 200 nm in size were oxidized, a series of intermediates with decreasing levels of Fe^{II} were obtained; the series corresponds to a magnetite/maghemite solid solution, the cell edge of which ranges continuously from 0.8338 to 0.8389 nm. The intermediates had the same crystal size and morphology as the original crystals. The intermediate with the highest level of Fe^{II} ($\text{Fe}^{\text{II}}/(\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}) = 0.30\text{--}0.19$), has XRD reflections (e.g. 110 or 210) which indicate a primitive cubic cell. The structure resembles that of lithium ferrite (LiFe₅O₈) in which the octahedral B site is split into two sites. The site with fourfold multiplicity is randomly occupied by $1\frac{1}{3}$ Fe^{III} and $2\frac{2}{3}$ vacancies, respectively, per unit cell. The other B site contains 12 Fe^{III} yielding the formula $\text{Fe}_8[\text{Fe}_{11/3}\square_{22/3}\text{Fe}_{12}]\text{O}_{32}$ (space group P4₃32) i.e. in the end member, maghemite, the lithium site is occupied by $1\frac{1}{3}$ Fe^{III} plus $2\frac{2}{3}$ vacancies. The formula ranges from $\text{Fe}_8^{\text{III}}[\text{Fe}_{11/3}^{\text{III}}\square_{22/3}\text{Fe}_{12}^{\text{III}}]\text{O}_{32}$ (ideal)

to $\text{Fe}_8^{\text{III}} [\text{Fe}_2^{\text{II}} \square_2 \text{Fe}_{12}^{\text{III}}] \text{O}_{32}$ depending on the level of Fe^{II} present. In the Fd3m structure, vacancy ordering with $2^{2/3}$ vacancies per unit cell is not possible because of the fractional number of vacancies. Tripling the cell along c is, thus, necessary and this results in a tetragonal space group (P4_12_12) and a formula of $\text{Fe}_{24}^{\text{III}} [\text{Fe}_{40}^{\text{II}} \square_8] \text{O}_{96}$. The tetragonal unit cell has $a = 0.833 \text{ nm}$ and $c = 2.501 \text{ nm}$ (i.e. $c = 3a$). Sometimes the tetragonal maghemite is referred to as the ordered form and the cubic material as the disordered form, but it should be noted that, in addition to a maghemite without vacancy ordering, there is also the cubic $\text{P4}_3 32$ phase with vacancy ordering (see Stanjek, 2000).

If the particles of the magnetite precursor are small ($< 100 \text{ nm}$), the resulting maghemite only shows reflections from the space group Fd3m. Goss (1988) oxidized nano-sized magnetite and found that at 200°C , a magnetite/maghemite solid solution (i.e. with some Fe^{II} present) was produced, whereas at 500°C , the maghemite was fully oxidized and had a primitive cubic cell with vacancy ordering.

Commercial maghemite (i.e. that used for recording devices) has the tetragonal unit cell. This material is obtained by a series of phase transformations via goethite, hematite and magnetite. The final stage is the diffusion-controlled, topotactic oxidation of the comparatively large (200 nm) crystals of Fe_3O_4 ; these crystals are large enough to permit complete ordering of the vacancies to take place (see Chap. 14).

Various authors have reported that maghemite contains ca. 2% water (as protons on the vacant octahedral sites) which is partly exchangeable with Na^+ and K^+ (Braun, 1952; Swaddle & Oltmann, 1980). They proposed that the formula be written as HFe_5O_8 . David and Welch (1956) suggested that in view of the high level of cation vacancies in the structure, the presence of water might have a stabilizing effect. Stanjek (2000) reported that the maghemites produced from OH-containing precursors, viz. from lepidocrocite, (by heating at 180°C and 250°C) and from goethite and ferrihydrite (by heating with sugar at 300°C and 400°C) had OH contents (as determined from the number of Fe deficient sites) of between 0.83 and 2.34 per formula unit, whereas maghemites formed from magnetites had only 0.16–0.58 OH per formula unit and a maghemite produced from hematite was OH-free. The degree of oxidation z of these samples was mostly 0.5–1 (Fig. 2.14).

During dehydroxylation of lepidocrocite, the water molecules leave the lepidocrocite crystals causing the crystals to break up, so that only tiny crystals of maghemite form (see Chap. 14). Because the crystals are so small, the vacancies are not ordered, hence the XRD pattern shows no superstructure lines. The $[001]$ and $[110]$ directions of the maghemite crystals parallel the $[001]$, and $[100]$ directions, respectively of the lepidocrocite crystals.

2.3.3.5 Wüstite Fe_{1-x}O

Although this compound has the nominal formula FeO , stoichiometric material cannot exist as a stable phase at low pressures or at pressures in excess of 10 MPa . The non-stoichiometry is accommodated by oxidation of a proportion of the metal ions and the creation of cation vacancies (Lindsley, 1976).

A stable, cation-deficient phase written as Fe_{1-x}O (with $1-x$ ranging from 0.83 to 0.95) exists at 0.1 MPa pressure and temperatures greater than 567°C . This phase

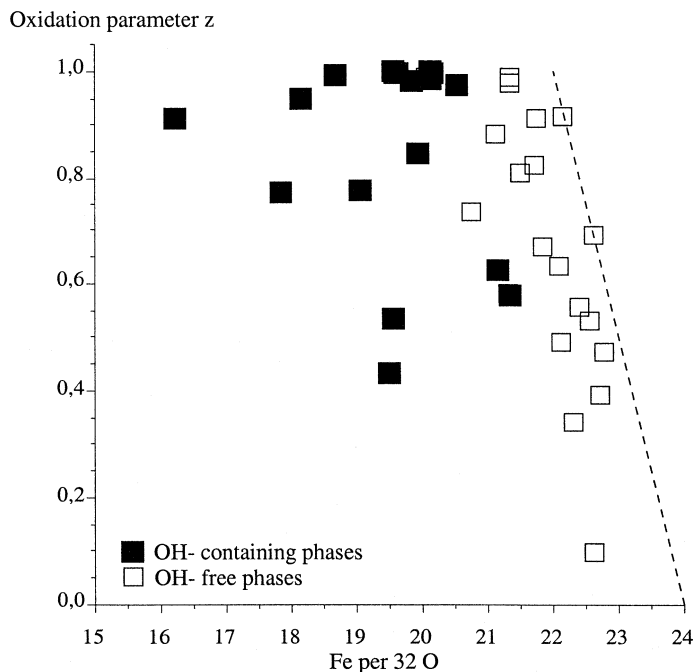


Fig. 2.14 Relationship between the oxidation parameter z and the Fe site occupancy per 32 oxygen (magnetite = 24; maghemite = 211/3) of magnetite/maghemite samples prepared from OH-free (magnetites, hematites) (□) and from OH-containing (lepidocrocite, goethite, ferrihy-

drite) (■) precursors by heating. $z = (1 - 2R) / (1 + 2/3 R)$, with $R = \text{Fe}^{\text{II}} / \text{Fe}^{\text{III}}$. The dashed line connects maghemite ($z = 1$) with magnetite ($z = 0$). (Courtesy H. Stanjek & N.Sabil; Sabil et al. in prep.; with permission).

disproportionates to Fe metal and Fe_3O_4 when cooled slowly to temperatures lower than 567 °C. At this temperature, the equilibrium curves of $\text{Fe}/\text{Fe}_{1-x}\text{O}$ and $\text{Fe}_{1-x}\text{O}/\text{Fe}_3\text{O}_4$ intersect. If, however, Fe_{1-x}O is rapidly quenched from the equilibrium region, the non-stoichiometric form can be obtained as a metastable phase at room temperature (Hentschel, 1970).

FeO has a defective NaCl structure. It can be regarded as consisting of two interpenetrating face centered cubic structures of Fe^{II} and O^{2-} . The cubic unit cell contains four formula units and, depending on the vacancy content, a ranges from 0.428–0.431 nm (Fig. 2.15). The density decreases with increasing vacancy level from 5.72 to 5.61 g cm⁻³ (Bogdandy & Engell, 1971). An alternative description of the structure is that of a ccp array of anions stacked along the [111] direction; planes of anions alternate with planes of cations. Most of the Fe is in octahedral interstices with a small proportion of Fe^{III} on the usually vacant tetrahedral sites. The octahedra share edges (Fig. 2.16a) and Fe^{II} – and O-layers alternate along [111] (Fig. 2.16b).

Single crystal X-ray diffraction and neutron diffraction studies of a quenched sample indicated that the vacancies were not spread statistically over the structure, but were arranged in clusters (Koch/Cohen clusters) consisting of 13 vacancies and four

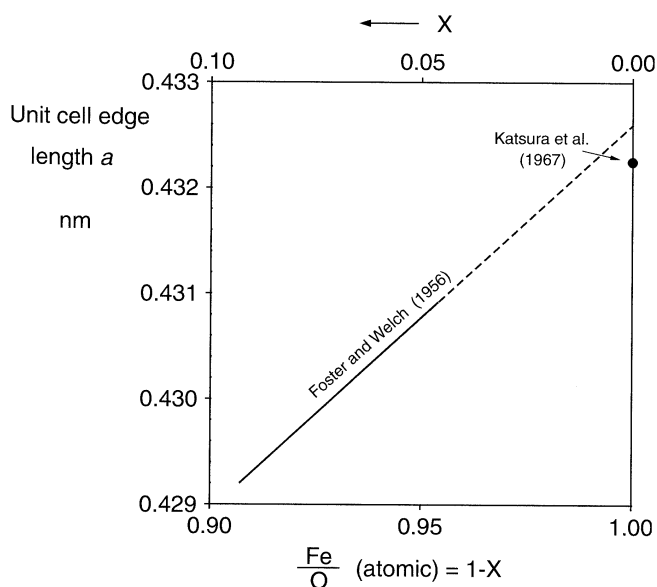


Fig. 2.15 Unit cell dimension of wüstite as a function of the composition (Lindsley, 1976, with permission). The solid line is based on data from Foster & Welch (1956). The data point from Katsura et al. (1967) was obtained at a pressure of 36 Kb.

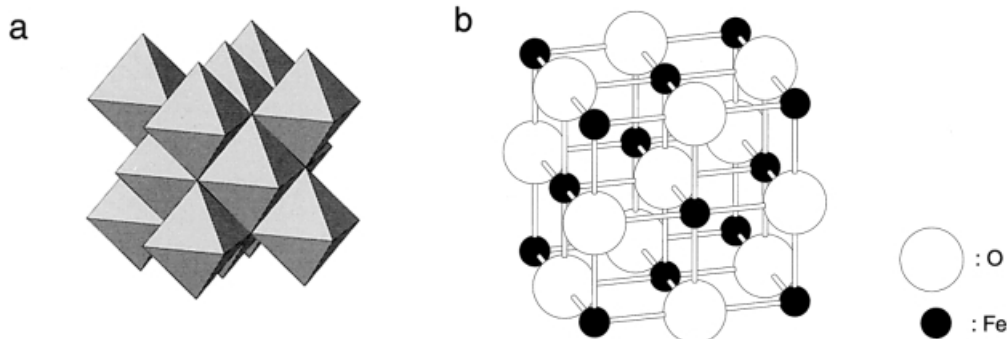


Fig. 2.16 Structure of wüstite (Stanjek, unpubl.). a) Arrangement of octahedra. b) Ball-and-stick model.

tetrahedrally coordinated cations (Koch & Cohen, 1969). Subsequent neutron diffraction studies on wüstite in the high temperature, equilibrium region indicated that the vacancy-to-interstitial ratio in this sample was 3–4:1. Based on these observations, a basic entity consisting of four vacancies, tetrahedrally coordinated to one interstitial Fe, i.e. a 4:1 cluster, has been proposed (Cheetham et al., 1971). Two or three of these basic clusters link by edge-sharing to form 8:3 and 6:2 clusters (Battle & Cheetham, 1979).

2.4

The Fe-Ti oxide system

There are structural analogues of a number of iron oxides in the Fe-Ti-O system. Under certain conditions, continuous solid solutions exist between the two members of a pair. The magnetite-ulvospinel and the hematite-ilmenite pairs are well-known examples. The principle in going from the Fe oxide to the Ti-containing phase is to replace two Fe^{III} by one Fe^{II} and one Ti^{IV} , thereby increasing the unit cell size.

Ulvospinel, Fe_2TiO_4 , has an inverse spinel structure with $a = 0.8536$ nm (Lindsley, 1965). Ti^{IV} and Fe^{II} are distributed over the tetrahedral sites. A continuous solid solution (called titanomagnetite) exists between the end members. This solid solution has the spinel structure with a ranging from 0.8393 to 0.8536 nm as the composition of the solution changes from $(1-x)\text{Fe}_3\text{O}_4$ to $x\text{Fe}_2\text{TiO}_4$ ($x = 0-1$). The cation distribution in this solid solution appears to depend on the temperature of formation and the rate of cooling. It can be described by at least four different models depending on the temperature of formation (Trestman-Matts et al., 1983).

A related system is that of the titanomaghemites, Fe_2TiO_5 , which are formed by oxidation of the titanomagnetites. These are spinels with vacancies in some of the cation positions. The detailed distribution of cations and vacancies is not fully understood; a discussion of the different models and possibilities is given by Lindsley (1976). A non-linear relationship between the unit cell size of titanomaghemite ($a = 0.8483$ nm) and that of maghemite ($a = 0.835$ nm) was matched by a non-linear increase in the Curie temperature from 80 to 450 °C (Dunlop & Özdemir, 1997).

Above 950 °C hematite and ilmenite, the other pair in the Fe-Ti-O system, form a continuous solid solution with the space group of hematite. At low temperatures, there is a large miscibility gap between the two end compounds (see Chap. 15). The presence of Fe^{III} and Ti^{IV} ions in ilmenite (FeTiO_3) was established using Mössbauer spectroscopy (Ruby & Shirane, 1961). Ilmenite has an ordered hematite structure with half the iron being replaced by Ti ions. There are alternating planes of Fe^{II} or Ti^{IV} along [001]. The unit cell of ilmenite has six layers and the edge lengths are $a = 0.50884$ nm and $c = 1.4085$ nm (Lindsley, 1965). The group symmetry is lower than that of hematite ($R\bar{3}$ instead of $R\bar{3}c$) and the number of crystallographically unequal sites has doubled.

Another structure in the Fe-Ti-O system is that of pseudorutile $\text{Fe}_2\text{Ti}_3\text{O}_8(\text{OH})_2$. This mineral appears to consist of intergrowths of goethite and rutile with a unit cell with $a = 0.2868$ nm and $c = 0.4607$ nm (Grey et al., 1983).

Appendix

Interplanar spacings for the iron oxide crystal systems.

The value of d , the perpendicular distance between adjacent planes in the set (hkl) , may be calculated using the formulae:

$$\text{Cubic} \quad \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$\text{Tetragonal} \quad \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

$$\text{Orthorhombic} \quad \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\text{Hexagonal} \quad \frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

$$\text{Monoclinic} \quad \frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

3

Cation substitution

3.1

General

As shown in Table 2.1, several of the Fe oxides have isostructural equivalents in which cations other than Fe occupy the interstices of the oxygen framework. The diaspora structure of goethite (α -FeOOH), for example, is adopted by diaspora (α -AlOOH) itself, groutite (α -MnOOH), bracewellite (α -CrOOH) and montroseite (VOOH). All these oxide-hydroxides exist as pure minerals although they are much rarer than goethite. Analogous synthetic phases with the diaspora structure are ScOOH and GaOOH. The various cations do not modify the structure, but they do affect the size of the unit cell (Muller & Joubert, 1974). In fact, a linear relationship exists between the volume of the orthorhombic unit cell of the MOOH forms and the ionic radius of the M^{III} cation for $M^{III} = \text{Al, Co, Cr, Ga, V, Mn, Fe and Sc}$ (Fig. 3.1). An analogous set of minerals exists for hematite (α -Fe₂O₃) which is isostructural with corundum (α -Al₂O₃), eskolaite (α -Cr₂O₃) and karelianite (α -V₂O₃) and for lepidocrocite (γ -FeOOH) which is isostructural with boehmite (γ -AlOOH). Phases isostructural with magnetite are Pb₃O₄, Co₃O₄ and Mn₃O₄.

The existence of these isostructural compounds suggests that solid solutions could be formed between two end members via isomorphous substitution for Fe^{III} by other cations.¹⁾ The likelihood of substitution depends on the similarity of the ionic radii and the valency of the cations (Goldschmidt, 1937). M^{III} is the most suitable cationic species and a radius about 18% higher or lower than that of high-spin Fe^{III} in sixfold coordination can be tolerated. Isomorphous replacement of Fe in Fe oxides by a number of cations has been observed in nature and, more frequently, in the laboratory. As far as is known, however, almost all these solid solutions have broad miscibility gaps, possibly induced by development of structural strain as substitution rises.

For the size of the unit cell of M^{III} substituted Fe^{III} oxides, a linear relationship between the Fe oxide and the appropriate structural analogue has been postulated. This is the so-called Vegard rule (Vegard, 1921). In practice, the change in unit cell parameters often deviates from the Vegard line, with the extent and direction of the deviation being different for different substituents and different unit cell parameters

1) The extent of substitution for Fe^{III} by a cation M is expressed here as $M/(\text{Fe}+M)$ in mol mol⁻¹; 0.1 mol mol⁻¹ is equivalent to 10 mol % substitution.

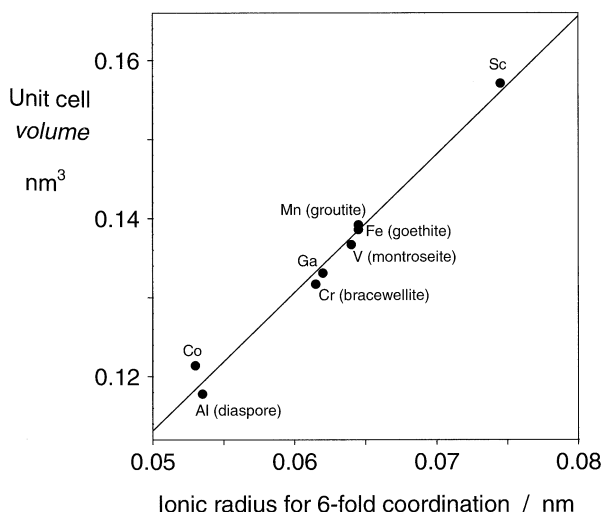


Fig. 3.1 Relationship between the unit cell volume of various MOOH minerals or synthetic compounds with the diaspoire structure and the ionic radius of M^{III} .

(v. Steinwehr, 1967). For oxides or oxide hydroxides produced at low temperature ($<100^\circ\text{C}$), deviations are attributed to structural imperfections created by the incorporation, in order to balance any cation deficit, of either OH (in the case of hematite) or extra OH (goethite) into the structure.

In addition to M^{III} cations, M^{II} and M^{IV} cations may also enter the Fe^{III} oxide structure, but uptake is usually less than 0.1 mol mol^{-1} . In addition to the ionic radius, the contribution by substituting cations to the crystal field stabilization energy (CFSE) and the change in lattice energy is considered to influence the tendency of such cations to replace Fe^{III} in Fe^{III} oxides (Dawson et al., 1985). Problems of charge balance arise with these cations and it has been assumed that a proportional uptake or release of protons could balance incorporation of di- and tetravalent cations, respectively (Bernstein & Waychunas, 1987; Cornell et al., 1992). For the incorporation of Pb^{IV} and Ti^{IV} , the development of a permanent positive charge balanced by the adsorption of ions has also been suggested (Fitzpatrick et al., 1978; Gerth, 1990). Of the metals considered so far, all replace Fe^{III} in the octahedral position. This is less likely for smaller ions such as Si^{IV} and P^V . It has been postulated for example, that Si (Campbell et al. 2002) and P (Galvez et al. 1999) occupy empty tetrahedral positions in the hematite structure.

A common method of synthesizing M-substituted oxides, particularly goethite and hematite is to add base to mixed M-Fe salt solutions to precipitate M-associated ferrihydrite. Most M^{II} ions do not change their oxidation state, but incorporation of Mn^{II} and Co^{II} in goethite is preceded by oxidation of these ions to the trivalent state (Giovanoli & Cornell, 1992). An indication of whether isomorphous substitution has occurred can be obtained from changes in the unit cell dimensions of the Fe oxides

(shown by XRD line shifts), by chemical analysis, Mössbauer, infrared and diffuse reflectance spectroscopy and, if the substituents are distributed randomly within the crystals, by dissolution. Congruent dissolution, i.e. the release of both host and guest ions at the same rate, has been demonstrated for some, but not all, synthetic substituted goethites, hematites, and magnetites (Fig. 3.2). Incongruent dissolution suggests that either a separate phase is present (assuming that this phase has a different dissolution rate from that of the Fe oxide) or that the substituents are concentrated towards the core or periphery of the crystal.

Various properties of Fe oxides change regularly with increasing substitution. Among these are the positions of the visible and infrared absorption bands, mag-

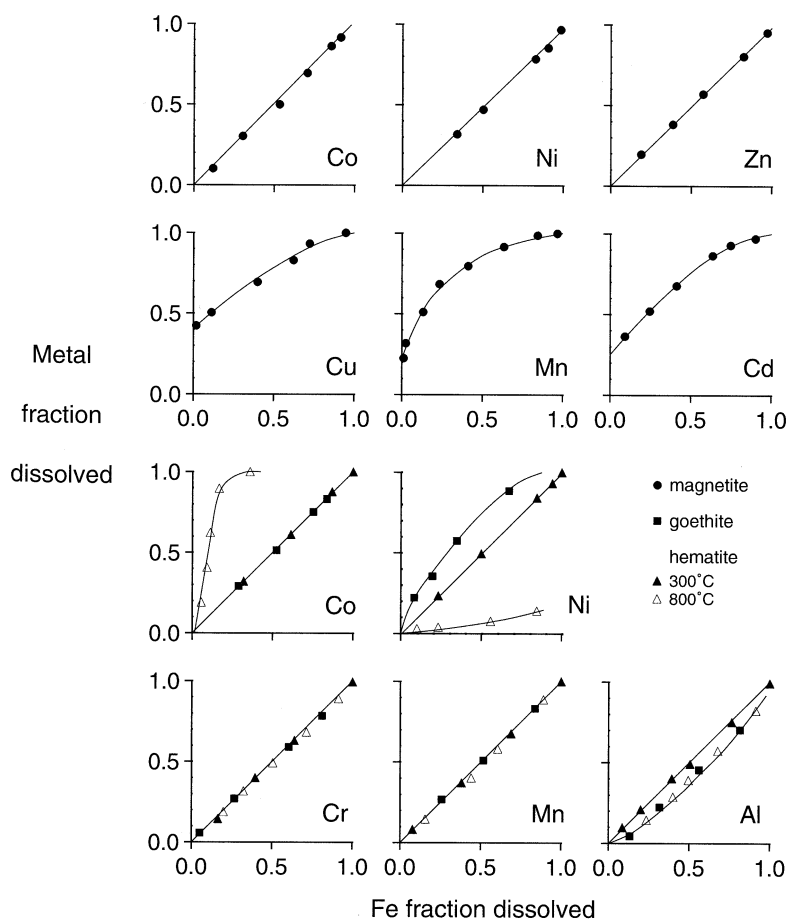


Fig. 3.2 Fraction of various metals released versus Fe released during acid dissolution of synthetic metal-substituted magnetites (upper six plots; Sidhu et al., 1978, with permission), goethites and hematites (lower plots; Lim-Nunez & Gilkes, 1987; with permission).

netic properties, dehydroxylation temperature, rate of acid and reductive dissolution and crystal size and aspect ratio. It is, however, often difficult to assign changes in a single property unequivocally to substitution because several properties may be modified simultaneously. For example, the magnetic hyperfine field, B_{hf} , of goethite decreases with increasing incorporation of the diamagnetic Al, but at the same time the crystals become smaller and this also lowers the hyperfine field, even at 4 K (Murad & Schwertmann, 1983). Multiple correlations, although usually highly significant, vary between different sample sets and, thus, do not allow the separate effects of the two parameters to be quantified (Van San et al. 2001).

Isomorphous substitution of iron oxides is important for several reasons. In the electronics industry, trace amounts (dopants) of elements such as Nb and Ge are incorporated in hematite to improve its semiconductor properties. Dopants are also added to assist the reduction of iron ores. In nature, iron oxides can act as sinks for potentially toxic M^{II} , M^{III} and M^{IV} heavy metals. Investigation of the phenomenon of isomorphous substitution has also helped to establish a better understanding of the geochemical and environmental pathways followed by Al and various trace elements. Empirical relationships (e.g. Fe and V) are often found between the Fe oxide content of a weathered soil profile and the levels of various trace elements. Such relationships may indicate similarities in the geochemical behaviour of the elements and, particularly for Al/Fe, reflect the environment in which the oxides have formed (see chap. 16).

3.2

Goethite and lepidocrocite

3.2.1

Al substitution

Goethite is by far the best studied example of an isomorphously substituted iron oxide and of the various possible substituents in both natural and synthetic samples, Al is the best known example. Although Al is 17% smaller than Fe^{III} , up to $1/3$ of the Fe^{III} in goethite can be replaced by Al: the full range of substitution of up to $0.33 \text{ mol mol}^{-1}$ is found in natural goethites. One reason for this is simply the ubiquity and abundance of Al in rocks and soils and its mobilization together with Fe during weathering. Although most of the Al subsequently is separated from Fe by forming Al-silicates (clay minerals), a significant proportion is always also incorporated into Fe^{III} oxides.

A linear relationship exists between the extent of Al substitution and the a and b edge lengths of the unit cell of *synthetic* goethites (Fig. 3.3, Tab. 3.1) produced by widely different methods (Thiel, 1963; Jonas & Solymar, 1970). The c edge length, however, deviates from the Vegard line with the deviation (c) often being greater with increasing degree of substitution (mol mol^{-1}), for example (Schulze & Schwertmann, 1984):

$$\Delta c = c - (0.4596 - 0.02 \text{ Al}) \quad (n = 57; r^2 = 0.672) \quad (3.1)$$

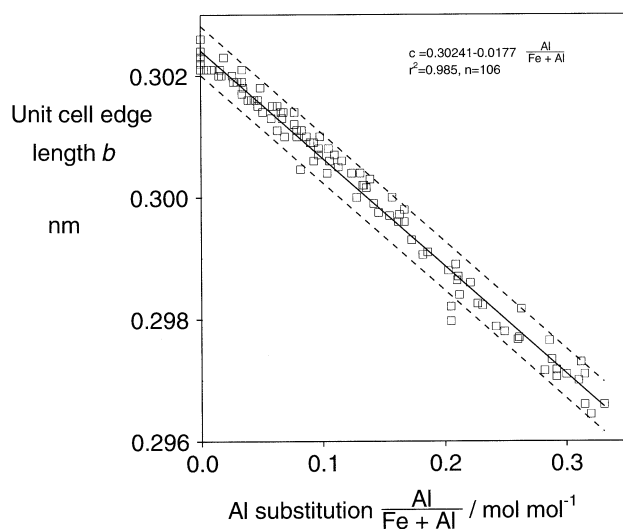


Fig. 3.3 Relationship between the edge length b of the unit cell and the Al-for-Fe substitution of synthetic goethites.

Tab. 3.1 Statistical parameters for relationships between structural Al and unit cell parameters of various Fe^{III} oxides.

<i>Samples</i>	<i>Range Al/(Fe+Al) mol mol⁻¹</i>	<i>Unit cell edge</i>	<i>Relationship intercept (nm)</i>	<i>slope (nm Al⁻¹)</i>	<i>n</i>	<i>r²</i>	<i>Ref.</i>
Synthetic goethites	0–0.33	<i>b</i>	0.3024	–0.0177	106	0.985	Unpubl.
Soil goethites	0–0.36	<i>b</i>	0.3026	–0.0207	84	0.924	1
Synthetic hematites (25 °C)	0–0.12	<i>a</i>	0.5039	–0.0146	59	0.88	2
Synthetic hematites (70 °C)	0–0.16	<i>a</i>	0.5038	–0.0152	10	0.972	3
Synthetic hematites (700 °C)	0–0.16	<i>a</i>	0.5036	–0.0148	8	0.994	4
Synthetic lepidocrocites	0–0.10	<i>a</i>	0.3071	–0.0180	8	0.994	5
Synthetic and soil maghemites	0–0.15	<i>a</i>	0.8343	–0.0222	28	0.825	6

1) Schwertmann & Carlson, 1994; 2) Schwertmann et al. 2000; 3) Schwertmann et al., 1979; 4) Da Costa et al. 2000; 5) Schwertmann & Wolska, 1990; 6) Schwertmann & Fechter, 1984;

At the same time, excess structural OH, which is considered to compensate for cation deficient sites, has been found. The general formula for Al substituted goethite $(\text{Fe}_{1-x}\text{Al}_x)_{y/3}\text{O}_{1-y}(\text{OH})_{1+y}$, takes this excess into account; y may be as high as 0.25 (Wolska & Schwertmann, 1993). Heating of goethites at up to 200 °C reduced the c edge length (by removal of extra H bonds), thereby shifting c towards the Vegard line (Schwertmann & Carlson, 1994).

As structural Al increases, the dehydroxylation temperature, the OH stretching frequency and both OH bending vibrations as well as their separation ($\delta\text{OH} - \gamma\text{OH}$)

increase (Schulze & Schwertmann, 1984; Cambier, 1986). The extent of these increases is counteracted by structural defects which increase with rising Al substitution. These defects probably arise both because Al affects the hydrogen bond across the double chains of octahedra and because the hydrogen bond has its strongest vector along the crystallographic *c*-direction (see Fig. 2.4 d,e). A suitable measure of the number of defects is the deviation from the Vegard rule of the *c* unit cell edge length (see above). The goethite crystals become smaller as Al substitution increases (Fig. 3.4) and change from large polydomainic crystals to smaller, monodomainic ones (Schulze & Schwertmann, 1987). This change may be associated with the rate of crystal growth which in 0.3M KOH at 70 °C, decreased linearly from 1.9 to

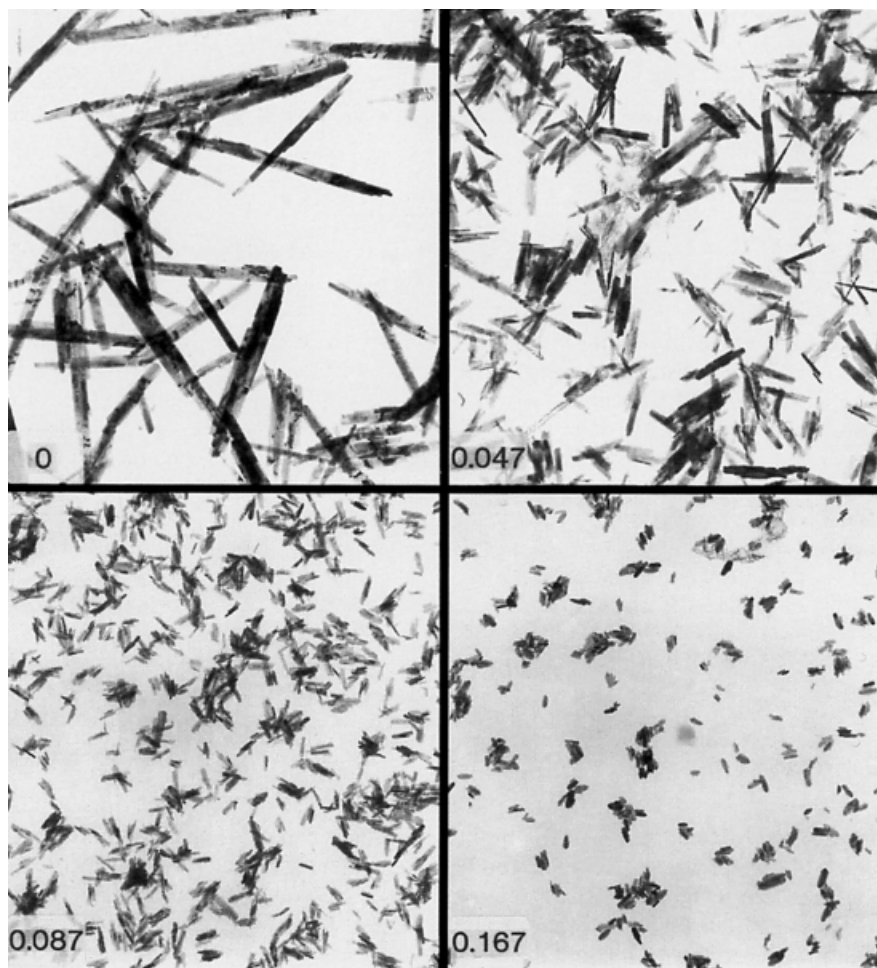


Fig. 3.4 Electron micrographs of goethites with Al substitution increasing from 0 to 0.167 mol mol⁻¹ (produced from 2-line ferrihydrite in alkaline solution at 70 °C).

$0.5 \cdot 10^{-3} \cdot \text{min}^{-1}$ as $[\text{Al}]$ in the system rose from 0 to 20 mmolL^{-1} (Schwertmann, unpubl.).

The magnetic hyperfine field (B_{hf}) decreases as structural Al increases. This is to be expected because the diamagnetic Al does not contribute to the magnetic field. Since, however, B_{hf} (T) is also reduced as the crystal size decreases (even at 4 K), both Al substitution *and* crystal size (here represented by mean coherence length perpendicular to (111), MCL_{111} , in nm) must be combined to account for the variation of B_{hf} satisfactorily, (Schwertmann & Murad, 1983) i.e.

$$B_{\text{hf}} = 50.65 - 4.2 \text{ Al}/(\text{Fe} + \text{Al}) - 8.7/\text{MCL}_{111} \quad (n = 20; r^2 = 0.969) \quad (3.2)$$

Again, although useful for indicating the general trend, relationships of this type are numerically valid only for the sample set for which they have been established (Vandenberge et al. 2000). Structural Al also reduces the dissolution rate of goethite in strong acids and in strong reductants such as dithionite (see Chap. 12, Fig. 12.20 & 12.22) (Schwertmann, 1984a; Torrent et al., 1987).

Under any set of conditions, pH and temperature, as well as $\text{Al}/(\text{Fe} + \text{Al})$ in the system, have a major effect on the amount of Al incorporation. pH is important because, among other things, it influences Al speciation in solution. For goethite produced from Al-ferrihydrite in alkaline media, there is, at any particular $[\text{OH}^-]$, a linear relationship between $[\text{Al}]$ in the system and structural Al in the final goethite (Fig. 3.5a). Because $[\text{OH}^-]$ determines the concentration of the major Fe species under these conditions, viz. $\text{Fe}(\text{OH})_4^-$, a plot of structural Al vs. $[\text{Al}]/[\text{Fe}(\text{OH})_4^-]$ eliminates the effect of $[\text{OH}^-]$ (Lewis & Schwertmann, 1979) (Fig. 3.5b). In strongly acidic media, Al exists as the unhydrolysed Al^{3+} ion and the high charge of this species may hinder Al incorporation. The lower charged species – AlOH^{2+} and $\text{Al}(\text{OH})_2^+$ – which are present under weakly acidic conditions or $\text{Al}(\text{OH})_4^-$ under alkaline conditions, appear, on these grounds, more suitable for structural incorporation. Increasing the temperature ($25\text{--}70^\circ\text{C}$) reduces Al incorporation (Schwertmann & Craciun, unpubl.) (Fig. 3.5) probably by speeding up crystal growth.

Another factor which influences substitution appears to be the valency of the iron precursor, i.e. Fe^{II} vs. Fe^{III} . At pH 7, aluminous ferrihydrite is converted mainly to Al-hematite. Owing to the high solubility of Al phases in highly alkaline media, goethite that forms from aluminous ferrihydrite at high pH contains relatively low levels of Al. Oxidative hydrolysis of Fe^{II} -ions at pH 7 (25°C), however, leads to goethite which can incorporate up to the maximum amount of Al ($\text{Al}/(\text{Fe} + \text{Al}) = 0.33$) (Schwertmann & Cornell, 1991). These goethite crystals are very small and poorly crystalline with a low magnetic hyperfine field at 4 K, e.g. 48.6 T for $\text{Al}/(\text{Fe} + \text{Al}) = 0.25$ compared with 50.6 T for bulk, pure goethite (Goodman & Lewis, 1981; Murad & Schwertmann, 1983).

Al-for-Fe substitution in *natural* goethites was originally discovered, with the aid of X-ray diffraction, in marine, oolitic, iron ores from the Jurassic era by Correns & von Engelhardt as early as in 1941 and twenty years later found in soils by Norrish and Taylor (1961). Since then, a large number of studies has revealed that Al substitution in goethites from the weathered zone, e.g. in soils (see chap. 16), appears to be the rule rather than the exception. It should be noted that Al located in the struc-

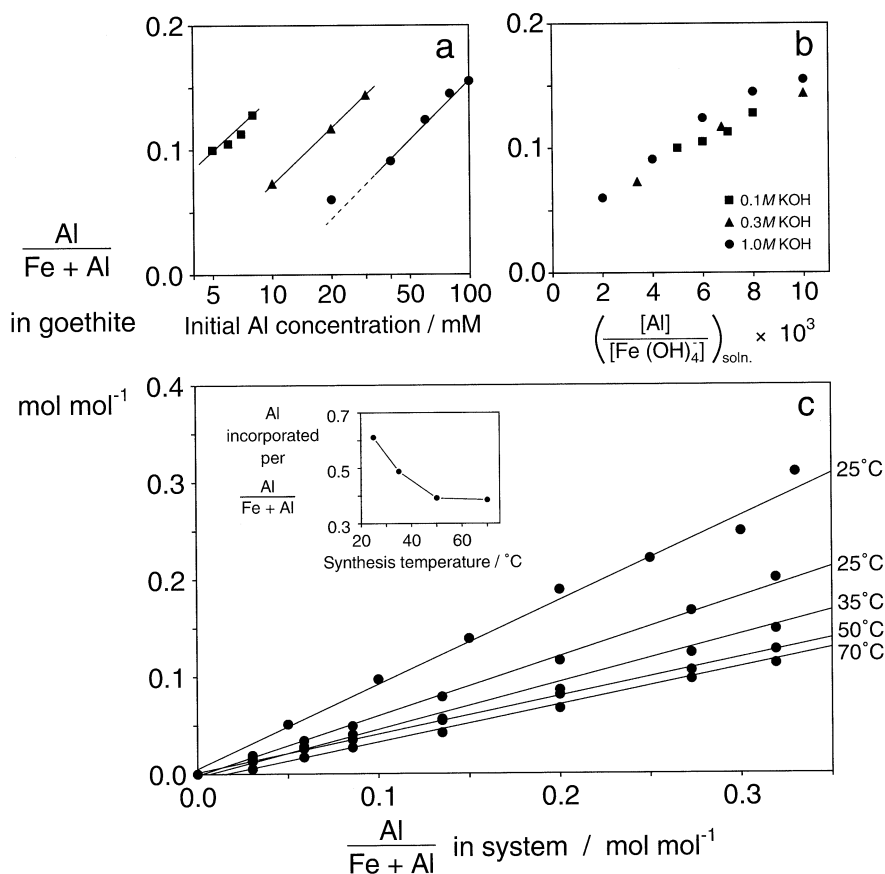


Fig. 3.5 The extent of Al incorporation into the structure of goethite. Effect of a) initial Al concentration; b) $\text{Al}/\text{Fe}(\text{OH})_4^-$; c) temperature. The insert in (c) shows the amount of Al incorporated per $\text{Al}/(\text{Fe} + \text{Al})$ in the system vs. synthesis temperature (a & b: Lewis & Schwertmann, 1979; with permission; c: Schwertmann & Craciun, unpubl.).

ture of goethite and hematite in bauxite (Al ores) cannot be extracted for Al metal production (Grubbe et al., 1981).

Oxidation of FeCl_2 solutions at pH 7–8 in the presence of soluble Al led to Al substituted *lepidocrocite* with an $\text{Al}/(\text{Fe} + \text{Al})$ of up to 0.14; the *a*, *b* and *c* unit cell edge lengths fell linearly as the Al content increased (Schwertmann & Wolska, 1990). The B_{hf} at 4.2K also decreased linearly over the same range of Al substitution, i. e.

$$B_{\text{hf}}(T) = 45.06 - 5.95 \cdot \text{Al}/(\text{Fe} + \text{Al}) \quad (n = 6; r^2 = 0.903) \quad (3.3)$$

(De Grave et al., 1995). In addition, Al substitution raised the temperature at which *lepidocrocite* transforms to *maghemite* (Van San et al. 2001).

3.2.2

Other substituting cations

A large number of cations besides Al can be incorporated into the goethite structure (Tab. 3.2). The substituting ions are all located on octahedral sites and except for Co^{III} , are in the high spin state. Table 3.3 lists the maximum observed cation substitution and the changes in the unit cell edge length a and the cell volume. The level of substitution can be related, at least in part, to the match between the radius and valency of the guest ion and those of Fe^{III} . Of the trivalent metal ions whose radii are close to 0.064 nm, substitution in synthetic goethite has been achieved for Mn, Cr and V. For the latter two ions, the magnitude of substitution is less than 0.1 mol

Tab. 3.2 Cations substituting for Fe^{III} in various Fe oxides

Oxide	Substituting cation
Goethite	$\text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$ $\text{Al}^{\text{III}}, \text{Cr}^{\text{III}}, \text{Ga}^{\text{III}}, \text{V}^{\text{III}}, \text{Mn}^{\text{III}}, \text{Co}^{\text{III}}, \text{Sc}^{\text{III}}$ $\text{Pb}^{\text{IV}}, \text{Ge}^{\text{IV}}$
Lepidocrocite	Al^{III}
Akaganéite	$\text{Cu}^{\text{II}}, \text{Si}^{\text{IV}}, \text{Mn}^{\text{III}}, \text{Ni}^{\text{II}}$
$\delta\text{-FeOOH}$	$\text{Mn}^{\text{III}}, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Mg}^{\text{II}}, \text{Ca}^{\text{II}}$
Hematite	$\text{Al}^{\text{III}}, \text{Cr}^{\text{III}}, \text{Mn}^{\text{III}}, \text{Rh}^{\text{III}}, \text{Ga}^{\text{III}}, \text{In}^{\text{III}}, \text{Nd}^{\text{III}}, \text{Ni}^{\text{II}}$ $\text{Cu}^{\text{II}}, \text{Ge}^{\text{IV}}, \text{Sn}^{\text{IV}}, \text{Si}^{\text{IV}}, \text{Ti}^{\text{IV}}$
Magnetite	$\text{Al}^{\text{III}}, \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Ca}^{\text{II}}, \text{Ge}^{\text{IV}}$
Maghemite	$\text{Al}^{\text{III}}, \text{Ti}^{\text{IV}}, \text{Sn}^{\text{IV}}$

Table 3.3 Cations substituting for Fe^{III} in goethite. Maximum substitution and corresponding unit cell parameters (references, see text)

Cation	Ionic radius* (nm)	Maximum substitution (mol mol⁻¹)	Unit cell edge length a (nm)	Cell volume (nm³)
Fe^{III}	0.0645	—	0.9956	0.1390
Al^{III}	0.0535	0.33	0.9800	0.1333
Cr^{III}	0.0615	0.10	0.9956	0.1384
V^{III}	0.064	0.06	0.9951	0.1386
Mn^{III}	0.0645	0.47	1.038	0.1390
Co^{III}	0.0545	0.10	0.9119	0.1367
Ni^{II}	0.0690	0.06	0.9976	0.1393
Cu^{II}	0.073	0.05	1.0013	0.1393
Zn^{II}	0.074	0.07	1.0007	0.1400
Cd^{II}	0.095	0.07	1.0067	0.1426
Pb^{IV}	0.0775	0.02	0.9977	0.1393

* Shannon & Prewitt (1969)

mol^{-1} . Goethite formed by storing a Nd-ferrihydrite coprecipitate in 0.3 M KOH at 40 °C contained no Nd (Nagano et al. 1999).

A linear change in unit cell parameters has been used to demonstrate structural incorporation of Mn (Stiers & Schwertmann, 1985; Ebinger & Schulze, 1989; 1990), Co (Cornell & Giovanoli, 1989; Gerth, 1990), Cr (Schwertmann et al., 1989) and Ni (Cornell et al., 1992). The pH influences the extent of Mn^{III} substitution. Mn-goethites grown from ferrihydrite at pH 12 at from room temperature to 70 °C contained up to 0.15 mol mol^{-1} Mn (Stiers & Schwertmann, 1985; Cornell et al., 1987; Vempati et al. 1995; Gasser et al. 1999). At pH 8, only 0.03 mol mol^{-1} Mn could be incorporated (Cornell et al. 1990), whereas, based on the shift of the unit cell b parameter, up to 0.47 mol mol^{-1} was incorporated at pH 6 and 50 °C (Ebinger & Schulze, 1990). Changes in the unit cell edge length b for Cr, Mn, Co and Al are shown in Figure 3.6.

Magnetic properties are also affected by substitution. The B_{hf} at RT decreased linearly from 38.3 T to 34.8 T as the $\text{Mn}/(\text{Fe} + \text{Mn})$ increased from 0 to 0.09 (Vempati et al., 1995). XAS analysis at the Mn-K_{α} and FeK_{α} edges showed that the local structure around Fe remains goethite-like up to the highest Mn substitution of 0.47 mol mol^{-1} , whereas that around Mn is goethite-like only up to an Mn substitution of 0.13 mol mol^{-1} . Above this level, groutite clusters are formed. The trivalency of Mn in the structure was shown by XANES analysis and is further proof that the Mn^{2+} was oxidized upon incorporation (Scheinost et al. 2001). Detailed atomic positions of the $\text{Fe}_{1-x}\text{Mn}_x\text{OOH}$ phases are also given in this study.

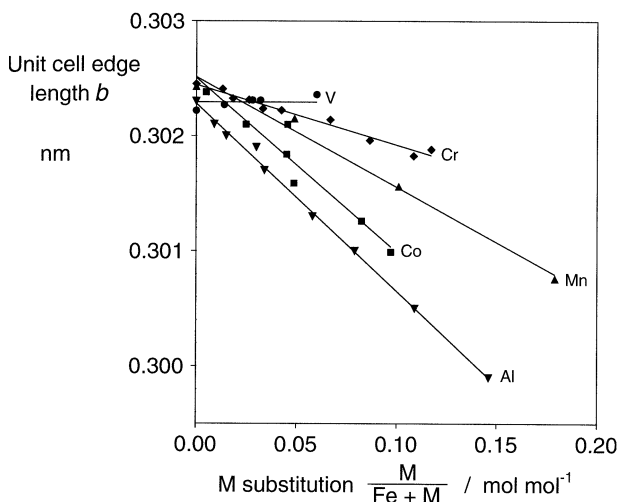


Fig. 3.6 Relationship between the unit cell edge length b of synthetic goethites and the level of structurally incorporated Al^{III} , Mn^{III} , Cr^{III} , Co^{III} and V^{III} (data from Schulze & Schwertmann, 1984; Stiers & Schwertmann, 1985; Schwertmann et al., 1989; Gerth, 1990 and Schwertmann & Pfab, 1994, respectively).

A factor which influences the extent of isomorphous substitution in goethite grown from M-ferrihydrites at high pH, is the degree of congruency of dissolution of M-ferrihydrite during its transformation to goethite (Giovanoli & Cornell, 1992). Release of Mn is congruent, hence Mn is fully taken up by the goethite structure. Co, Ni and Zn are released from ferrihydrite more slowly than Fe, so the residual ferrihydrite becomes increasingly enriched in the guest ion. Nucleation and most growth of goethite is completed before the rest of the metal enriched ferrihydrite transforms and as a result, a proportion of the guest ion is located at the surface or in the surface layers of the goethite crystals. Acid dissolution showed that distribution of these elements in goethite was in line with what was predicted from the dissolution kinetics of the ferrihydrite precursor. In both phases, the distribution of Mn was uniform, whereas Co and even more so, Ni were concentrated in the outer layers of the crystals; substitution of these elements was less than $0.06 \text{ mol mol}^{-1}$. However, rastered EDAX (beam diameter 30nm) suggests that Mn substitution within a single acicular crystal falls linearly from the core to the edge, i.e. incorporation is not entirely homogeneous (Gasser et al. 1999).

Although Fe^{III} and Mn^{III} have similar ionic radii, Mn^{III} does not fit as readily into the goethite structure as does Fe^{III} because owing to its four d electrons, Mn^{III} has a tetragonally distorted coordination sphere on an octahedral site (*Jahn-Teller effect*). This distortion is reflected in an *increase* in the *a* edge length as the level of Mn substitution increases, and a decrease in the *b* edge length.

A close relationship exists between the *a* cell edge length of goethite and the extent of incorporation of Cd, Zn, Cu, Ni, and Co (Gerth, 1990) (Fig. 3.7 top): the rate of diminution or enlargement of *a*, i.e. the slope of the lines, can for certain valencies be linearly related to the ionic radius of these cations (Fig. 3.7 bottom). As little as $0.005 \text{ mol mol}^{-1}$ Cd substitution was detected by EXAFS (Spadini et al. 1994). EXAFS spectra also revealed that structural Ni led to a contraction along the edge-sharing double chains of octahedra and an expansion between them. It is suggested that structural distortion is reduced by this anisotropic relaxation (Manceau et al. 2000). For vanadium, a change in unit cell size of synthetic V-containing goethites cannot be measured because the ionic radii of Fe^{III} and V^{III} are almost identical (0.0645 vs. 0.064 nm). The congruent dissolution of V and Fe in synthetic and natural goethites in 6 M HCl at 25°C , however, strongly suggests that incorporation of V in the goethite structure has taken place (Fig. 3.8, right) (Schwertmann & Pfab, 1994 & unpubl.).

Mixtures of cations can also be incorporated in the goethite structure. In experiments with mixtures of equal amounts of Ni & Mn, Co & Ni, and Co, Ni & Mn in the system, the goethite formed took up 0.054 and $0.08 \text{ mol mol}^{-1}$ Ni and Mn, 0.055 and $0.07 \text{ mol mol}^{-1}$ Ni and Co and 0.02 , 0.04 and $0.043 \text{ mol mol}^{-1}$ Ni, Mn and Co, respectively (Cornell, 1991). The dissolution behaviour of the multi-substituted goethites paralleled that of the singly substituted goethites (Fig. 3.8, left) (Giovanoli & Cornell, 1992) with Mn release being congruent and Co and Ni release being incongruent (Cornell, unpubl.).

As in the case of Al, other cations which replace Fe^{III} also modify goethite properties. The yellow colour of pure goethite turns reddish upon incorporation of Cr^{III} ,

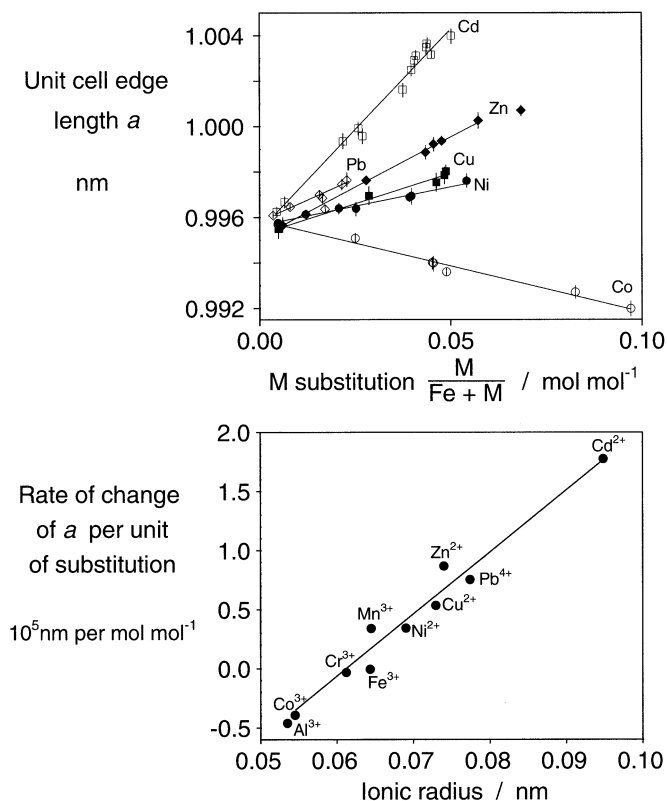


Fig. 3.7 Top: Relationship between the unit cell edge length a of synthetic goethites and various structurally incorporated metals. Bottom: Rate of change of a per unit of substituted metal (= slope of the upper curves) vs. ionic radius of the respective metal cations (Gerth, 1990, with permission).

olive to greyish with Mn^{III} and greenish with V^{III} (see Plate 6.II). The dissolution rates decreased in the order, Mn-goethite, pure goethite, V-goethite, Al-goethite, Cr-goethite (Fig. 12.23, see also Lim-Nunez & Gilkes, 1987). The presence of the substituting cation (particularly Mn and Co) can modify the ratio of length-to-width (i.e. the aspect ratio) of the acicular goethite crystals and this, in turn, can influence the magnetic coercivity of the $\gamma\text{-Fe}_2\text{O}_3$ which is produced from goethite and used in magnetic recording devices.

Nothing is known about whether anions can enter the structure of synthetic goethites. Under ambient conditions in an aqueous system, Si interferes with the crystallization of goethite in both acid and alkaline media but, so far, no analytical proof of incorporation in the structure has been obtained (Glasauer, 1995). Furthermore, there is hardly any information about the replacement of Fe in *natural* goethites by cations other than Al and by anions. Congruent release of Fe with V^{III}

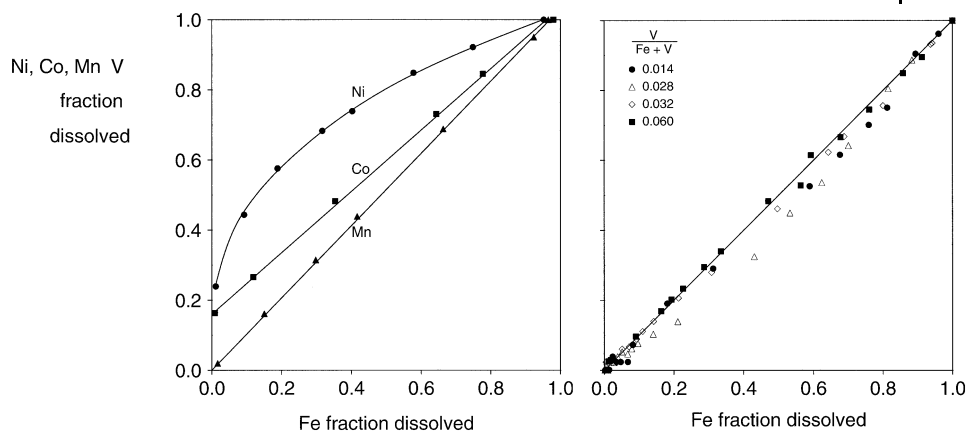


Fig. 3.8 Fraction of metals dissolved vs. fraction of Fe dissolved from synthetic metal substituted goethites. Left: Ni-, Co- and Mn-goethites in 0.5 M HCl at 75 °C (Giovanoli & Cornell, 1992, with permission). Right: Four synthetic V-goethites in 6 M HCl at 25 °C (Schwertmann & Pfab, 1994, with permission).

and Cr^{III} as well as the trivalency of the vanadium, suggested that the latter cations occupy a structural position in goethites from Sudanese laterites (Schwertmann & Pfab, 1996). Yapp and Poths (1986, 1992) and Yapp (1987) described ca. 20 natural, well crystallized goethites containing 0.0066–0.013 mol mol⁻¹ carbonate and used the $^{13}\text{C}/^{12}\text{C}$ ratio to gain information about the earth's atmosphere during the formation of these oxides.

An attempt to incorporate Cr into *lepidocrocite* does not appear to have been successful (Morales et al., 1990).

3.3

Hematite

3.3.1

Al substitution

As for goethite, the solid solution with its isostructural analogue corundum, (α - Al_2O_3) is the best known example of substitution. Al substitution in soil hematites is very common especially in tropical soils as is the association of Al-hematite with Al-goethite (see Chap. 16). A range of Al-hematites produced under different conditions, was investigated as early as 1925 (Forestier & Chaudron, 1925). Other early, systematic studies were carried out by Cailliere et al. (1960), Gastuche et al. (1964) and v. Steinwehr (1967). Their Al-hematites were produced from Al-ferrihydrites, Al-goethites or Al-lepidocrocites. Not only is the extent of Al-for-Fe substitution, but also a range of other properties, interdependently affected by the synthesis condi-

tions. The hematites are, therefore, usually described by multiple correlations with interdependent variables; a number of these is given below.

The key variable influencing Al substitution at a given Al concentration in the system, and also the other properties, is synthesis temperature. When hematite is produced at below 100 °C, up to 1% of the Fe positions can be replaced by Al, whereas higher substitution can be achieved by heating Al-goethites to 500–600 °C. At even higher temperatures (900–1000 °C), however, part of the Al is again expelled from the structure and crystallizes as corundum; $\text{Al}/(\text{Fe}+\text{Al})$ in hematite is thereby lowered to <0.15 (v. Steinwehr, 1967; De Grave et al., 1982; Wells et al. 1989). Al-hematites produced by heating Al-goethites at up to 500 °C contained up to 0.28 mol mol⁻¹ Al. At 700 °C no more than 0.18 mol mol⁻¹ was retained and at 900 °C the maximum level was 0.12 mol mol⁻¹ with Fe-substituted corundum being formed as well (Wells et al. 1989).

For Al-substituted hematites produced at <100 °C, there was a linear and significant relationship between incorporated Al and the a edge length (Tab. 3.1), but not for the c edge length, probably because of stacking faults which occur along the c -axis. As for the Al-goethites, the intercepts of the regression line for a vs. $\text{Al}/(\text{Fe}+\text{Al})$ is higher and the slope is lower, the lower the temperature of synthesis (Fig. 3.9, left). This effect has been ascribed to the presence of structural OH, probably located at Fe deficient sites. By taking the loss on ignition (LOI in mg g⁻¹), as a possible measure of structural OH, into account, the substitution/unit cell dimensions relationships for Al-hematites produced at 40, 65 and 90 °C are substantially improved as shown by the following equations which relate the effect of Al substitution to changes in a (nm), c (nm) and V (nm³) ($n = 48$) (Stanjek & Schwertmann, 1992):

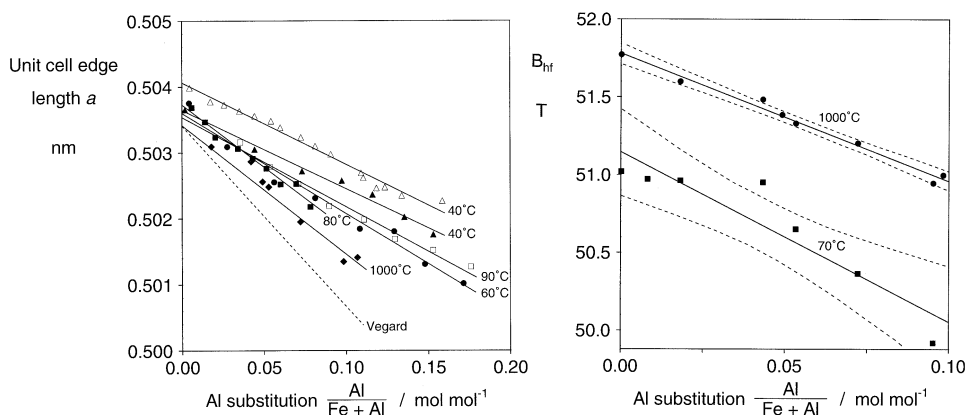


Fig. 3.9 Effect of Al-substitution in synthetic hematites on; (Left) the unit cell edge length a of hematites synthesized at various temperatures (Stanjek & Schwertmann, 1992, with permission), and (Right) the magnetic hyperfine field B_{hf} of hematites formed at 70 °C and 1000 °C; dotted lines indicate 95% confidence limits (Murad & Schwertmann 1986; with permission).

$$a = 0.5036 - 0.0183 \text{ Al}/(\text{Fe} + \text{Al}) + 1.75 \cdot 10^{-3} \text{ LOI}; \quad (r^2 = 0.852) \quad (3.4)$$

$$c = 1.374 - 0.0512 \text{ Al}/(\text{Fe} + \text{Al}) + 1.30 \cdot 10^{-3} \text{ LOI}; \quad (r^2 = 0.806) \quad (3.5)$$

$$V = 0.3018 - 0.0512 \text{ Al}/(\text{Fe} + \text{Al}) + 0.49 \cdot 10^{-2} \text{ LOI}; \quad (r^2 = 0.869) \quad (3.6)$$

Although statistically significant, the r^2 values are not very high. This is partly due to the variety of conditions under which the hematites are prepared. In other words, a higher degree of significance is obtained for samples prepared in the same way, especially at the same temperature because the temperature affects the amount of structural OH. Therefore, after removing all the OH by heating to ca. 1000 °C, a single line is obtained for a and for c irrespective of the way in which the hematites were synthesized. A higher degree of significance with single correlations was also obtained for Al-hematites produced by heating Fe-Al-oxinates at 700 °C because the crystal size was >100 nm (Da Costa et al. 2001); the respective equations are:

$$a = 0.5036 - 1.484 \cdot 10^{-4} \text{ Al}/(\text{Al} + \text{Fe}); \quad (r^2 = 0.994); \quad (3.7)$$

$$c = 1.3750 - 5.368 \cdot 10^{-4} \text{ Al}/(\text{Al} + \text{Fe}); \quad (r^2 = 0.983); \quad (3.8)$$

Al substitution strongly affects the magnetic hyperfine properties. As Al substitution increased, both the Néel and the Morin temperatures (see Chap. 6) and the magnetic hyperfine field (B_{hf}) decreased. Again, B_{hf} increased and the data scatter was reduced when the crystallinity was improved by heating to 1000 °C (Fig. 3.9, right). Alternatively, the correlation between B_{hf} (T) and Al-substitution for less well crystallized hematites ($n = 15$) can be improved by taking the crystal size (MCL_c = mean coherence length in c -direction, nm) into account in addition to Al substitution (Murad & Schwertmann, 1986), i.e.

$$B_{\text{hf}} = 51.7 - 7.6 (\text{Al}/\text{Fe} + \text{Al}) - 33/\text{MCL}_c; \quad (r^2 = 0.889) \quad (3.9)$$

The B_{hf} of the well crystalline Al-hematites produced by heating Fe-Al-oxinates at 700 °C ($n = 8$) showed a much higher correlation with Al-substitution (da Costa et al. 2001):

$$B_{\text{hf}} (\text{RT}) = 51.65 - 0.061 \text{ Al}/(\text{Al} + \text{Fe}); \quad r^2 = 0.994; \quad (3.10)$$

$$B_{\text{hf}} (80\text{K}) = 54.08 - 0.032 \text{ Al}/(\text{Al} + \text{Fe}); \quad r^2 = 0.975; \quad (3.11)$$

As substitution by Al, a paramagnetic diluent, increased from 0.046 to 0.15 mol mol⁻¹, the mass magnetic susceptibility was lowered from 183.8×10^{-8} to 41.9×10^{-8} m³ kg⁻¹ and the saturation isothermal remanent magnetization (SIRM) at 800 mT fell from 14.8 to 1.84 mAm² kg⁻¹ (Wells et al. 1999).

TEM and differential X-ray line broadening (expressed by the ratio of the width at half height of the 104 relative to that of the 110 reflection) indicate that the thickness of the platy Al-hematite crystals decreases as Al/(Fe + Al) increases (Schwertmann et al., 1977; Barrón et al., 1984). It is this change in morphology, rather than the structural Al, which governs the IR spectra, in particular the shape factor and the absorp-

tion maxima of the A_{2u} and the E_u vibrations (see Chap. 7). Furthermore, structural Al makes hematites lighter in colour, i.e. closer to that of corundum, as measured by the Munsell colour value or the lightness of the CIE colour system (see Chap. 6) (Barrón & Torrent, 1984). As with Al-goethites, the IR band at 548 nm for Al hematites shifts to lower wave lengths in the second derivative of the reflectance spectrum (Kosmas et al. 1986; Scheinost et al. 1999).

Six Al-hematites with an $Al/(Al + Fe) = 0.002\text{--}0.10$ were produced from Al-lepidocrocites via Al-maghemites by heating at 652 °C for 24 hr (Van San et al. 2001):

Their BET surface areas (S in m^2/g) increased with Al-substitution according to:

$$S = 10 + 200 (Al/(Al + Fe)); \quad r^2 = 0.98; \quad (3.12)$$

whereas for B_{hf} (T) at RT, the correlation was substantially improved by taking MCL_{104} (nm) also into account:

$$B_{hf} = 51.7 - 6.6 (Al/(Al + Fe) - 13.3/MCL_{104}); \quad r^2 = 0.98; \quad (3.13)$$

The ratio of the band amplitude at 485–500 nm to that at 542–574 nm increased linearly from 0.1 to 0.5 as the Al-substitution increased from 0 to 0.10 mol mol⁻¹ ($r^2 = 0.95$).

3.3.2

Other cations

Other cations which can replace Fe in the hematite structure are listed in Table 3.2; they refer essentially to synthetic hematite. Mn can replace up to 0.05 mol mol⁻¹ Fe in hematite synthesized from ferrihydrite at pH 8 (Cornell & Giovanoli, 1987, 1990). Because of the Jahn-Teller effect, Mn^{III} for Fe substitution is significantly limited (Singh et al. 2000). The presence of Mn-hematite in a Tunisian soil was suggested on the basis of a lowered B_{hf} (Vandenberghe et al., 1986). Up to 0.09 mol mol⁻¹ of Cu can be incorporated (Cornell & Giovanoli, 1988). Dissolution of Cu-hematite was congruent. Modification of the unit cell parameters was observed for Mn-hematite (produced from Mn-goethite) (Vandenberghe et al., 1986), Cu-hematite (Cornell & Giovanoli, 1988; Kandori et al. 1998), Ni-hematite (Cornell et al., 1992) and Cr-hematite (v. Steinwehr, 1967; Kandori et al. 1998). Around 0.03 mol mol⁻¹ Ni raised the mass magnetic susceptibility (Wells et al. 1999). Von Steinwehr (1967) produced a complete solid solution series for $(Fe,Cr)_2O_3$ with a strong positive deviation from the Vegard line for a and a negative deviation for c (see also DiCerbo & Seybolt, 1959). The deviation was interpreted as a superposition of a geometrical (due to the difference in ionic size) on a chemical component (chemical interaction due to differences in electronegativity). If the substituents are non-statistically distributed in the structure, the geometrical effect will be reduced and the chemical effect will be strengthened (v. Steinwehr, 1967a). Hematites produced by forced hydrolysis of Fe^{III}-solutions at 100 °C in the presence of Cu and Cr also contained OH in the structure as seen from FTIR spectra (Kandori et al. 1998). Analogously, the incorporation

of $0.06 \text{ mol mol}^{-1} \text{ Ni}^{\text{II}}$ in hematite led to an increase in the unit cell volume from 0.301 to 0.303 nm^3 , and created structural OH (seen by FTIR) to compensate for the charge deficit (Singh et al. 2000).

As with Al, the Morin transition was suppressed for hematites containing Ga, Cr, In (see Fig. 6.9), Mn, Ti and Zn, whereas a sharp increase occurred with Rh incorporation (Coe & Sawatzky, 1971).

Low levels of structural Ge^{IV} have also been observed in natural hematite from the Apex mine, Utah (Bernstein & Waychunas, 1987) and to achieve charge balance, incorporation of two Fe^{II} for one Ge^{IV} , i.e. similar to the two Fe^{II} for one Ti^{IV} in ilmenite, has been suggested. Synthetic, single crystals of Ge substituted hematite have also been grown by a chemical vapour transport method (Sieber et al. 1985). A range of elements including Zr, Ce, Hf, V, Nb, Ta, W and Pb has been used as low level dopants ($2 \cdot 10^{-4} - 0.2 \text{ g kg}^{-1}$) to improve the semiconductor behaviour of hematite anodes (Anderman & Kennedy, 1988). The increase in unit cell c from 1.3760 to 1.3791 nm and in a from 0.50378 to 0.50433 nm indicated that Nd^{III} (as an inactive model for trivalent actinides of similar ionic size (Am^{III} : $r = 0.0983 \text{ nm}$; Nd^{III} : $r = 0.098 \text{ nm}$)) was incorporated in the structure (Nagano et al. 1999).

The possibility of Si incorporation into hematite was tested by Campbell et al. (2002). Heating Si-ferrihydrite coprecipitates at 672°C in a DTA apparatus produced hematites whose unit cell volume increased regularly from 0.30186 to 0.30213 nm^3 up to an $\text{Si}/(\text{Si} + \text{Fe})$ of ca 0.07 ; this was paralleled by a decrease in the Fe site occupancy from 11.5 to 11.1 per unit cell (instead of 12 for an ideal cell) probably in order to balance structural Si. Heating these hematites to 800°C lowered B_{hf} (RT) in a regular fashion from $51.65(0)\text{T}$ at 0 Si to $51.16(0)\text{T}$ as $\text{Si}/(\text{Si} + \text{Fe})$ rose to 0.07 . Furthermore, no Morin transition took place even at 4.2K at an $\text{Si}/(\text{Si} + \text{Fe})$ of ≥ 0.05 . At an $\text{Si}/(\text{Si} + \text{Fe})$ of ≥ 0.134 , part of the incorporated Si was ejected and formed a separate Si-Fe phase which was paramagnetic at 4.2K and visible in the XRD trace as a broad peak at $0.25 - 0.35 \text{ nm}$.

Galvez et al. (1999) demonstrated that phosphorus up to a P/Fe mol ratio of $0.03 \text{ mol mol}^{-1}$, can be incorporated into the hematite structure by heating P-containing 2-line ferrihydrite. Support for structural incorporation comes from a higher unit cell c ($1.3776 \Rightarrow 1.3824 \text{ nm}$), IR-stretching bands of P-OH, a lowered intensity ratio of the XRD $104/113$ lines and congruent release of Fe and P upon dissolution. It is suggested that P occupies an empty tetrahedral position. Yubero et al. (2000) claim, on the basis of Rutherford backscattering spectroscopy, that up to $0.04 \text{ mol mol}^{-1}$ of Ar could be incorporated in the structure of hematite prepared from $\text{Fe}(\text{CO})_5$ by ion beam assisted deposition in the presence of O_2^+ and Ar^+ , followed by annealing at 500°C .

3.4

Magnetite and maghemite

Substitution of a large range of cations can be readily induced in magnetite and maghemite because tetrahedral as well as octahedral positions are available. Sidhu et al.

(1978) synthesized substituted *magnetites* containing up to 0.01 transition metals at 90 °C. Dissolution curves indicated that Co, Ni and Zn were randomly distributed within the structure and replaced octahedral Fe^{II}. In contrast, Cu, Mn and Cd appear to be concentrated near the surface of the crystals. After conversion of these magnetites to maghemite, an outer zone free from trace elements was formed around the crystal indicating that oxidized Fe had migrated outwards and formed a new maghemite layer leaving the trace elements in the core (Sidhu et al., 1980). When the magnetite was converted to hematite, the divalent trace elements were ejected (because of their valency and size) and concentrated in the surface layers of the oxide, whereas Cr and Mn, which are compatible with the corundum structure, remained in the hematite.

Substituted magnetites prepared at pH 12 from ferrihydrite contained more than 0.1 mol mol⁻¹ Mn, Cu, Co or Ni (Cornell & Giovanoli, 1987, 1988, 1989; Cornell et al., 1992; Regazzoni and Matijevic, 1983). The products ranged from magnetites with low levels of substitution up to the fully substituted MFe₂O₄ (ferrites). For Co-substituted magnetites there appears to be a continuous variation in surface area and interfacial properties with increasing substitution (Ardizzone et al., 1987). There has been considerable interest in ferrites themselves, owing to their applications in electrical appliances, as catalysts and, because Co-ferrites are radioactive, corrosion products in water cooled nuclear power stations. Magnetites with Ca substitution of 0.19 mol mol⁻¹ and a corresponding increase in the cubic cell edge from 0.839 to 0.847 nm were prepared by De Siller et al. (1977).

Aluminium substitution in magnetite was first demonstrated by Michel in 1949 through a decrease in the unit cell size and a fall in the Curie point. A series of Al-magnetites was synthesized over the temperature range from 25 to 90 °C (Schwertmann & Murad, 1990). These magnetites were partly oxidized which places them structurally between magnetite, maghemite and hercynite (FeAl₂O₄). The unit cell edge length was related to the level of structural Al and Fe^{II} by the following equation:

$$a \text{ (nm)} = 0.83455 + 0.00693 \text{ Fe}^{\text{II}} - 0.00789 \text{ Al} \quad (n = 34; r^2 = 0.922) \quad (3.14)$$

At an Al/O₄ mol ratio of approximately 0.4, Al preferentially replaces tetrahedral Fe^{III} (A-site). Ardizzone et al. (1983) reported that magnetite prepared in sodium acetate buffer solution contains up to 2.3 mg g⁻¹ Na in the structure.

Al-maghemites were first produced by Michel (1949) by heating Al-substituted magnetites. The maghemites contained up to 0.33 mol mol⁻¹ Al which reduced the unit cell size from 0.832 nm to 0.808 nm. Al-maghemites were also synthesized by sequentially heating Al-ferrihydrite, reducing it to Al-magnetite and then reoxidizing the magnetite. An Al substitution of up to 0.1 mol mol⁻¹ was obtained and the edge lengths of the tetragonal unit cell were reduced: *a* dropped from 0.834 to 0.831 nm and *c* dropped from 2.502 to 2.490 nm (Wolska & Schwertmann, 1989b). Al atoms and vacancies were distributed between tetrahedral and octahedral sites. External field Mössbauer spectra of Al-maghemites formed by heating Al-lepidocrocites at 300 °C also suggested that Al was distributed over both sites (da Costa et al., 1994). The temperature of conversion to hematite increased from 550 to 750 °C as the level of Al substitution increased.

Six, highly substituted Al-maghemites (unit cell size 0.8348–0.8146 nm), produced in sequence by heating Fe-Al oxalate to give hematite, reducing the hematite to magnetite and oxidizing the magnetite to maghemite, showed the following relationships between B_{hf} (at 4.2 K in an applied field of 6T) and Al-substitution (Da Costa et al. 1996):

$$\text{A-site: } B_{hf}(T) = 52.0 - 3.0 (\text{Al}/(\text{Al} + \text{Fe})); \quad (r^2 = 0.98) \quad (3.15)$$

$$\text{B-site: } B_{hf}(T) = 53.1 - 2.6 (\text{Al}/(\text{Al} + \text{Fe})); \quad (r^2 = 0.96) \quad (3.16)$$

The Curie temperature was lower by ca. 150 K at a substitution of ca. 0.1 mol mol⁻¹ (DaCosta et al. 1996).

Al-substituted maghemites are also found in soils (see chap. 16), especially in those formed from basic igneous rocks. Al substitution of up to 0.15 mol mol⁻¹ reduced the *a* edge length from 0.8345 to 0.831 nm (Taylor & Schwertmann, 1974; Schwertmann & Fechter, 1984) (Tab. 3.2). Those maghemites found close to the surface were formed from Al-substituted goethite by firing (see Chap. 16). Al-substituted maghemites also occur, however, at greater depths in tropical soils, where heating is less likely (Goulart et al. 1998; da Costa et al. 1999). Their genesis has not yet been explained. Substitution of Fe by tin and titanium (0.08 mol mol⁻¹) was shown by EXAFS at the Sn and Ti K-edge and by a doublet in an RT Mössbauer spectrum which is not present in pure maghemite. Both tetravalent ions occupy octahedral sites in the structure (Helgason et al. 2001).

3.5

Other Iron oxides

Extensive replacement of Fe by transition metal cations and alkaline earth ions has been reported for δ -FeOOH (Okamoto, 1968). Muller et al. (1979) found incorporation of up to 0.4 mol mol⁻¹ Ca; solid solutions with the formula $\text{Fe}_{1-x}\text{K}_x\text{O}_{1-x}(\text{OH})_{1+x}$ could be identified. Jiménez-Mateos et al. (1990) reported that Co and Mn, respectively, could replace up to 0.3 and 0.5 mol mol⁻¹ Fe. The unit cell parameters decreased in both cases with increasing substitution. These Mn- and Co-substituted δ -FeOOHs decomposed at 200 °C to give poorly crystalline, substituted hematites.

Akaganéite can incorporate up to 0.06 mol mol⁻¹ Cu and much smaller amounts of Cr, Mn, Co, Ni and Zn in the structure (Inouye et al., 1974; Holm, 1985; Buchwald & Clarke, 1989). Incorporation of Al, Cr and Ga has also been reported (Lorenz & Kempe, 1987). Cornell (1992) produced akaganéite from acid Si-containing Fe^{III} solutions and found by congruent dissolution that up to 0.04 mol mol⁻¹ Si could be incorporated. The Si species were probably located in the tunnels (0.5 nm²) of the akaganéite structure.

Numerous coprecipitates of *ferrihydrite* with different cations (and anions) have been synthesized and exist in nature, but so far, no definite proof of structural incorporation has been produced, probably because of the very low particle size and crystallinity of the (2-line) ferrihydrite which makes the distinction between a position at



the surface and within the structure difficult. There is, however, some indirect evidence for substitution. For example, coprecipitated Si and some transition metal ions retard the conversion of ferrihydrite to goethite and/or hematite and do so to a much greater extent than do the same ions that were merely added (adsorbed on) to ferrihydrite afterwards. The effect of these transition metal ions has been correlated with the covalency of the Fe–O–M bonds in ferrihydrite (Giovanoli & Cornell, 1992). Furthermore, more M-substituted magnetite formed from coprecipitates of divalent transition metal ions with ferrihydrite than from ferrihydrite to which the same amount of metal ions had been added *after* precipitation. In addition, the DTA behaviour of Si-ferrihydrite coprecipitates shows a marked difference to that of ferrihydrite to which silicate solution has been added with the coprecipitate displaying greater thermal stability; IR data has suggested the presence of Fe–O–Si linkages (Carlson & Schwertmann, 1981; Campbell et al. 2002; Cornell & Giovanoli, unpubl.). The magnetic blocking temperature of synthetic, Si-containing ferrihydrites was lowered from ca 180 K for a Si content of 28.2 g Si kg⁻¹ to 65 K for a Si content of 55.4 g Si kg⁻¹ (Schwertmann et al. 2002). EXAFS data suggest that Au^{III} in Au-ferrihydrite is present as an outer-sphere complex (Berrodier et al. 1999).

Natural, As-rich Fe oxides with ca. 500 g Fe and up to 76 g As per kg from the coral reef of Amberlite Island, Papua-New Guinea were reported (Pichler et al. 1999) and similar compounds were synthesized in the laboratory; both these samples showed two broad XRD peaks akin to, but shifted, with respect to those of 2-line ferrihydrite, to higher spacings and higher average quadrupole splitting (Rancourt et al. 2001; Carlson et al. 2002). These results suggest that the Si and As are distributed throughout the ferrihydrite and may lead to even smaller particles and/or lower order. This also applies to the incorporation of natural dissolved organic matter (DOM) (Schwertmann et al. unpubl.).

A small amount of Cr^{III} could be incorporated in *wüstite* at 1350 °C (Bogdandy & Engell, 1971) and MgO and MnO were completely miscible with FeO: the mixed phases are important in the reduction of iron ores. *Wüstite* can be doped with small amounts of Mn, Mg, Ca and <10 g kg⁻¹ Si or Al to promote reduction (Moukassi et al., 1984). In *green rust* Fe^{II} has been replaced by Ni^{II} (Refait & Genin, 1997) and by Mg (Refait et al. 2001).

4

Crystal morphology and size

4.1

General

Properties of iron oxides such as IR spectra and magnetic and dissolution behaviour may be influenced by crystal morphology (growth form) and crystal size. Certain morphologies are desirable for industrial applications. Needles of maghemite are required for magnetic tapes because they can be orientated in a strong magnetic field during the manufacturing process and this reduces background noise during recording. On the other hand, iron oxide pigments for use in paints should be cubic because they tend to orient themselves with the brush stroke. Considerable effort has, therefore, been directed towards producing iron oxides with well defined habits and, where possible, uniform size or size distribution both for industrial pigments and to provide model substrates for studies of the adsorption of pollutants and other species. The range of shapes and sizes displayed by iron oxides reflects, to a large extent, the growth environment. Numerous *in vitro* studies have, therefore, also been carried out to relate the morphology of the synthetic and natural compounds to their growth environment.

4.1.1

Crystal growth

Detailed information about crystal growth is available in the books by Sunagawa (1987) and Mullin (1993). A very brief summary of the topic is provided here. Crystal growth from solution involves a number of steps. They are:

- Bulk diffusion of solvated ions or molecules to the surface of the crystal
- Adsorption at and diffusion over the crystal surface.
- Partial or total dehydration, dehydroxylation, decharging and/or rearrangement of the ions at the surface
- Integration of the ions into the structure.
- Counter diffusion of released solvent from the crystal.

The overall rate of growth depends upon the slowest step in this sequence. Crystal growth may be controlled either by the transport processes or by the chemical reaction at the surface. The mechanism of growth and the resulting crystal morphology

depend upon solution conditions, in particular the supersaturation and also on the structure of the growing crystal surface.

Under conditions of low supersaturation (low driving force conditions) nucleation/growth proceeds via dislocations (Burton-Cabrera-Frank (BCF) mechanism). With moderate supersaturation growth results from a two dimensional nucleation/spreading mechanism; nucleation on a flat face is fairly likely, but still rate limiting. At high levels of supersaturation, there is abundant nucleation on the crystal surface and the rate of growth is limited by the rate of diffusion of new material to the crystal surface.

The structure of the growing surface is characterized by the roughness factor or α factor (Bourne & Davey, 1976). The α factor is a function of the enthalpy of melting and the bonding energies of the crystal. It influences the growth mechanism that operates. When $\alpha < 2$, the surface is rough on a molecular level, nucleation proceeds readily and diffusion is rate determining. A high α value (>5) corresponds to a smooth surface with a high energy barrier to nucleation at low supersaturations. At intermediate values, two dimensional nucleation and spreading is the most likely growth mechanism. Interfaces tend to become rougher as supersaturation increases.

4.1.2

Crystal morphology

The *habit or morphology*¹⁾ is the external shape of the crystal. The faces which enclose a crystal and give it its characteristic habit can be grouped into forms, i.e. sets of crystal faces which are underlain by ions or atoms in the same geometrical relationship and which have, therefore, the same relationship to the crystal symmetry elements. Such a set of planes is enclosed in curly brackets. The general form of a crystal corresponds to a group of faces which intersects all the crystal axes. All other forms present in a crystal are termed special forms. For example, hematite and goethite have a number of forms (Tab. 4.1), whereas magnetite octahedra display only one form, viz. {111}. A single form is permissible for magnetite because the {111} planes enclose all space (closed form)²⁾.

Forms are frequently denoted by letters. By convention, the pinacoids that cut the *a*-, *b*- and *c*-axes are referred to as the *a*, *b* and *c* forms, respectively, and the {111} and {101} forms are *p* and *m*, respectively. In most other cases, the lettering is arbitrary having been chosen by the person who first described the crystal. The angles between the different faces will, however, remain constant and this assists in assigning a crystal to its symmetry class (Tab. 4.1). Because of the arbitrariness of the lettering it will not be used in this book.

1) Strictly speaking, morphology and habit are not identical. Morphology comprises such characteristics as crystal system, cleavage, twinning and specific crystal faces present as well as shape, whereas habit is the appearance resulting from the length-to-width ratio of the different faces.

2) An open form is one which does not enclose all space as for example the two parallel {001} faces (pinacoids) for goethite. An open form must be combined with at least one other form to enclose a crystal.

Tab. 4.1 Morphological characteristics of major iron oxide minerals

<i>Oxide</i>	<i>Axes</i>	<i>Forms</i>	<i>Angles</i>		<i>Twin plane</i>	<i>Cleavage</i>
Goethite	3 twofold	{100}	100/201	47.43	{210}	Perfect on {100}
		{101}	100/101	65.33		
		{201}	100/210	62.50		
		{210}				
		{211}				
Lepidocrocite	3 twofold	{010}	001/101	51.27	none	Perfect on {010}
		{001}				Good on {100}
		{102}				Less perfect on {001}
		{100}				
		{130}				
		{131}				
Hematite	1 threefold	{001}	101/001	12.42	{001}	none
		{101}	012/001	57.64	{102}	Parting along
		{101}				{001} & {101}
		{110}	104/001	38.28		
		{012}	113/001	61.25		
		{104}	116/001	42.34		
		{018}				
		{113}				
		{223}				
		{247}				
Magnetite	4 threefold	{111}			{111}	none Parting along {111}

Sources: Hurlbut (1959); Kostov (1968)

The observed morphology of a crystal is usually the *growth* morphology. The equilibrium morphology¹⁾ is rarely observed. Crystal morphology is governed by the rates at which the different faces grow and depends on a number of factors. The first of these is the *arrangement of ions* in the crystal, i.e. the symmetry of the unit cell. According to the Bravais law (1849), the morphological importance of a crystal face is proportional to its reticular density, i.e. the concentration of lattice points on the face. This, in turn, is directly proportional to the interplanar spacing; i.e. close packed planes tend to grow more slowly. As fast growing faces are eliminated quite rapidly, it is the slow growing faces which dominate the morphology. Donnay and Harker (1935) modified the original Bravais law to take into account the space group of the substance and showed that planes that would be systematically absent according to the laws of X-ray diffraction, are not morphologically important.

Morphology also depends on the *driving force* or chemical potential difference (μ/kt) in the crystallization process; this is related to the supersaturation of the system. A low driving force favours polyhedral crystals, whereas with a very high driving

1) $\Sigma\gamma A$ = minimum where A is the surface area and γ the surface free energy of a particular face. The equilibrium morphology corresponds

to the total free energy of the crystal in equilibrium with its surroundings (constant pressure and temperature) being a minimum.

force, dendritic, spherulitic or “bow-tie” morphologies tend to predominate (Sunagawa, 1987 a). Spherulites are quite often observed for lepidocrocite. In addition to the supersaturation, other aspects of the *growth environment*¹⁾ that influence morphology include local currents in solution, changes in the nature of the solvent and the presence of foreign ions. The morphology of hematite precipitated by forced hydrolysis of Fe^{III} solutions is particularly sensitive to these parameters. Both adsorbed and incorporated foreign ions can alter the relative free energies of different crystal faces and their growth rates and hence modify crystal habit. In some cases, low levels of impurities enhance the growth of a particular face, whereas higher levels block growth. The solvent influences the interfacial energy and the surface roughness factor. Local variations in growth environment may result in unequal development or malformation of the different faces of a growth form and hence a distorted morphology. The angles between the different faces remain constant, however, and this assists in assigning even a malformed crystal to its symmetry class. In the extreme case, and particularly in low-temperature, natural environments, there is hardly any distinct morphology by which the iron oxide can be identified.

Iron oxide crystals may be twinned. A twinned crystal is one in which there are two or more sections in each of which the structure has a different orientation, but which are related in a particular geometric manner. The surface which separates the two sections is termed the composition plane. Contact twins contain a regular composition plane, whereas when this plane is irregular, interpenetrant twins result. Twinned crystals have a higher energy than untwinned crystals; the energy difference between the two types is, however, often not very great. Twinning may be induced by impurities in the system.

Twinned crystals can be classified by shape, by type of growth or according to the symmetry element by which the different sections of the twin are related. In a *rotational* twin, the two or more sections can be made coincident by rotation about an axis. If this twin axis is parallel to the composition plane, the crystal is termed a parallel twin, whereas if the twin axis is perpendicular to the composition plane, a normal twin results. *Reflection* twins are those in which the two individual sections may be made coincident by reflection across a plane – the twin plane. *Mimetic* twins are those in which repeated twinning has given the crystal an apparently higher degree of symmetry than that possessed by the structure. These types of twins are all *composite* twins. Goethite also displays *epitaxial* twinning. Epitaxy is the case where crystals of one phase grow on the surface of another phase so that the first phase has a definite orientation with respect to the second (Bernal & Mackay, 1965). The essential requirement for epitaxy is a suitable match (<20% difference) between the interplanar spacings of the two phases.

4.1.3

Crystal size

As with the habit the crystal size may also vary considerably. It reflects growth conditions and determines the surface area which in turn, is important for all types of sur-

1) Most morphologies referred to here were obtained in solution.

face reactions. Usually the crystal size of iron oxides lies in the range of several nm to a few μm .

There are various methods of measuring the size of such small crystals. Visual observation by electron microscopy requires the measurement of a large number of single crystals (ca. 100) to obtain a representative size distribution. The crystal height can be obtained by shadowing the crystals.

An average crystal size can also be obtained from XRD line broadening using the Scherrer formula which describes the corrected width of an XRD line at an angle θ as a function of the mean size of the coherently scattering domain perpendicular to the hkl plane MCL_{hkl}

$$\text{MCL}_{\text{hkl}} = \frac{K\lambda}{b \cos \theta} \quad (4.1)$$

where λ is the X-ray wave length, b the true width of the X-ray peak at its half height and K is a shape factor (Klug & Alexander, 1974). To obtain the true width the experimental width must be corrected for the instrumental width. It should be stressed that the Scherrer formula measures the domain size and therefore underestimates the true crystal size for multidomainic crystals. Furthermore, the Scherrer formula does not consider the contribution of structural strain to line broadening. This restriction is overcome with a line profile analysis of Warren (1969) for which, however, a large particle standard ($> 1 \mu\text{m}$) showing only instrumental line broadening is required. This method enables the effect of strain to be separated from that of particle size and supplies information about the particle size distribution.

The size and size distribution of small particles of superparamagnetic Fe oxides can be estimated from Mössbauer spectra by recording the transition from the doublet spectrum into a magnetically split spectrum as the temperature decreases. The temperature of such a transition decreases as the particle size decreases. Other methods of particle size analysis are low angle X-ray diffraction and light scattering (Penners, 1985). A critical comparison of the different methods has been made for hematite by Amelse et al. (1981). Another comparison of various methods (TEM, XRD, Mössbauer spectroscopy, magnetometry) using Fe oxide catalysts with particles $< 10 \text{ nm}$ in size gave reasonably good agreement between the methods (Ganguly et al., 1993).

4.2

The iron oxides

These sections are mainly concerned with synthetic iron oxides. The morphologies of Fe oxide crystals in rocks, soils and biota are described in Chapters 15, 16 and 17. Table 4.2 provides an overview of the common crystal habits of the various Fe^{III} oxides.

Tab. 4.2 Habits of iron oxides

<i>Oxide</i>	<i>Principal habits</i>	<i>Other habits</i>
Goethite	Acicular	Stars (twins), hexagons, bipyramids, cubes, thin rods
Lepidocrocite	Laths	Tablets, plates, diamonds, cubes
Akaganéite	Somatoids, Rods	Stars, crosses (twins), hexagons, prisms*
Schwertmannite	“hedge-hog” aggregates	
δ -FeOOH	Plates	Thin, rolled films
Feroxyhyte	Plates	Needles
Ferrihydrite	Spheres	
Hematite	Hexagonal plates Rhombohedra	Spindles, rods, ellipsoids, cubes, discs, spheres, double ellipsoids, stars, bipyramids, peanuts,
Magnetite	Octahedra	Intergrown octahedra (twins), rhombic dodecahedra, cubes, spheres, bullets
Maghemite	Laths or cubes**	Plates, spindles

* Reported; no micrographs available (cf. Nightingale & Benck, 1960; Wolf et al., 1967).

** Adopts the morphology of its precursor.

4.2.1

Goethite

4.2.1.1 General

Although goethite displays a range of shapes and sizes, there is essentially one basic morphology – acicular. Acicular goethite crystals can range in length from a few tens of nm to several microns. Macroscopic crystals of natural goethite can be up to several mm in length although these may not be single crystals in a strict sense. A feature of goethite samples is the broad size distribution; monodisperse suspensions require special preparative methods.

The forms displayed by goethite crystals are depicted in Figure 4.1. The better developed the crystal, the more of these forms may be present. For example, the prismatic macrocrystal shown in Figure 4.2 was formed hydrothermally in a quartz geode and is particularly rich in forms. Additional faces, viz. 010, 120, 111, and 101 were also found on natural goethite crystals from Cornwall. Atomic Force Microscopy examination of these crystals showed growth, dissolution and cleavage features (Rakovan et al. 1999). Natural crystal aggregates occur in botryoidal, foliated, fibrous, concretionary, oolitic, massive and earthy textures.

Synthetic, acicular, goethite crystals are elongated along the [100] direction (*a*-axis) and often terminate in {210} faces (Fig. 4.3). This morphology appears to have been adopted in response to the double chains of corner shared octahedra which run parallel to the [010] direction and dominate the goethite structure. Crystal growth appears to proceed most readily by addition of growth units at the ends of these chains, i. e. in the *a*-direction. The {100} faces grow fast and, therefore, disappear quickly in

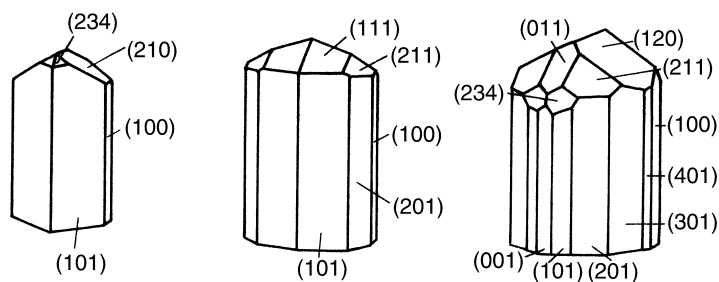


Fig. 4.1 Crystal forms of goethites (Ramdohr & Strunz, 1978; with permission; Peacock, 1942, with permission).

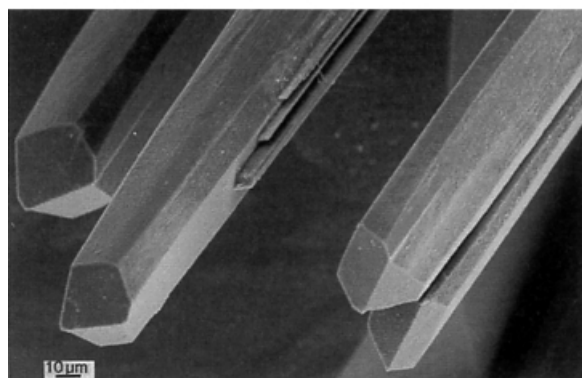
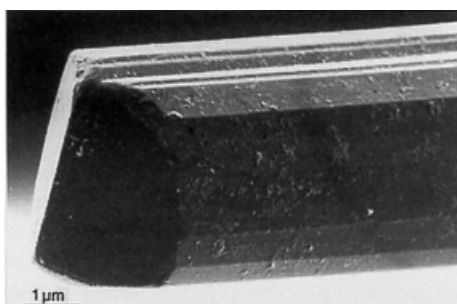


Fig. 4.2 Large goethite crystal formed hydrothermally in a quartz geode terminated by (210) faces (Courtesy R. Giovanoli).

favour of the {210} faces. In the early stages of the reaction, goethite crystals develop their thickness in the c -direction and thereafter grow in the a - and b -directions (Lewis & Schwertmann, 1980). Under conditions of very rapid growth and/or in the presence of impurities, long, thin needles with a high aspect ratio¹⁾ form.

The size and morphology of goethite crystals grown at pH 12 is related to the ageing history of the parent iron solutions (Atkinson et al., 1968). As the extent of hydro-

¹⁾ The aspect ratio is the ratio of crystal length to crystal width.

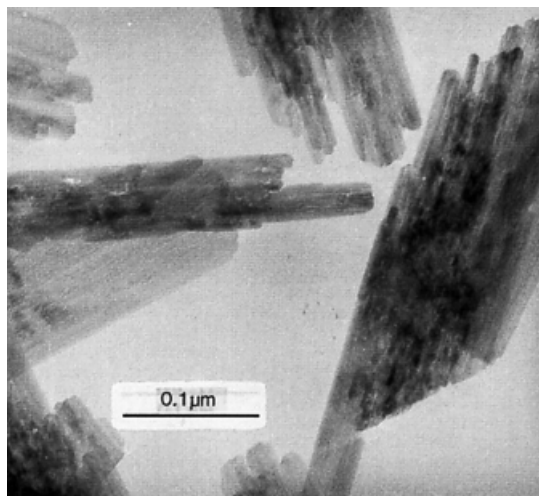


Fig. 4.3 Common acicular, polydomainic goethite crystals terminated by (210) faces (see Schwertmann et al. 1985).

lysis of the pre-aged solutions increases, both crystal size and extent of twinning are reduced. Increased hydrolysis promotes formation of numerous nuclei which then grow when the system is precipitated to pH 12.

For a long time it was tacitly assumed, on the basis of TEM and electron diffraction data, that the predominant crystal faces of acicular goethite were {001}, {100} and {010} i.e. that the cross section was rectangular (Atkinson et al., 1968; Cornell et al., 1974). Several models of the reactive surface groups have been based on this assumption. Subsequent TEM examination of ultrathin sections of goethite (both natural and synthetic) taken perpendicular to the [100] direction, showed, however, that the crystals have, in general, a diamondlike cross section (Smith & Eggleton, 1983; Schwertmann, 1984a; Van der Woude et al., 1984; Cornell & Giovanoli, 1986). Thus, the enclosing forms are predominantly {011} with {102} at the ends of the crystal. The large twin shown in Figure 4.4 illustrates this situation.

A cross section of a synthetic goethite grown from 2-line ferrihydrite in alkaline solution is shown in Figure 4.5. This high magnification photo shows (100) lattice fringes (≈ 1 nm) perpendicular to the long (a -) axis of the crystal and (011) lattice fringes (0.42 nm) parallel to the outer boundaries (only visible in the original photo) indicating that the enclosing faces are {011}. The same was found for a natural goethite, a thin section of which is shown in Figure 4.6. If the needles are very short they may stand upright on the grid and thereby expose their diamond-shaped cross section (Fig. 4.7; left). This is particularly the case where the goethites formed in partially neutralized Fe^{III} solutions at pH < 1.5 (Atkinson et al., 1968; Murphy et al., 1976; Mørup et al., 1983; Koch et al., 1986; Glasauer et al. 1999).

Although when examined using optical or even electron microscopy, crystal surfaces appear smooth, this is rarely the case. Techniques such as AFM and STM and optical interference methods (see Chap. 7) show that both growth and cleavage surfaces consist of terraces separated by steps which can be as little as one atomic layer



Fig. 4.4 Large goethite twin bounded by (101) side faces and (210) terminal faces (Schwertmann & Pfab, 1994, with permission; Schwertmann & Cornell, 2000, with permission).

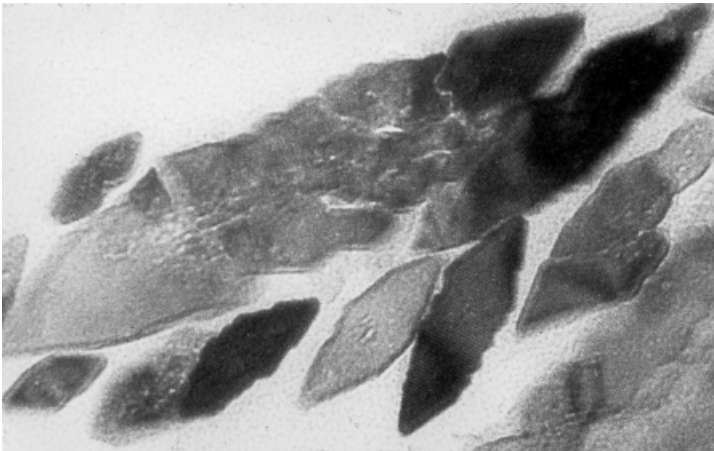


Fig. 4.5 High resolution electron micrograph of synthetic goethite crystals cut perpendicular to the needle axis [010]. The crystals are bounded by {101} faces. The large crystal contains faults and some of the smaller, fault-free crystals show ca. 1 nm lattice fringes corresponding to the a -parameter of the unit cell (0.9956 nm) (Schwertmann, 1984, with permission, courtesy H. Vali, Schwertmann & Cornell, 2000, with permission).

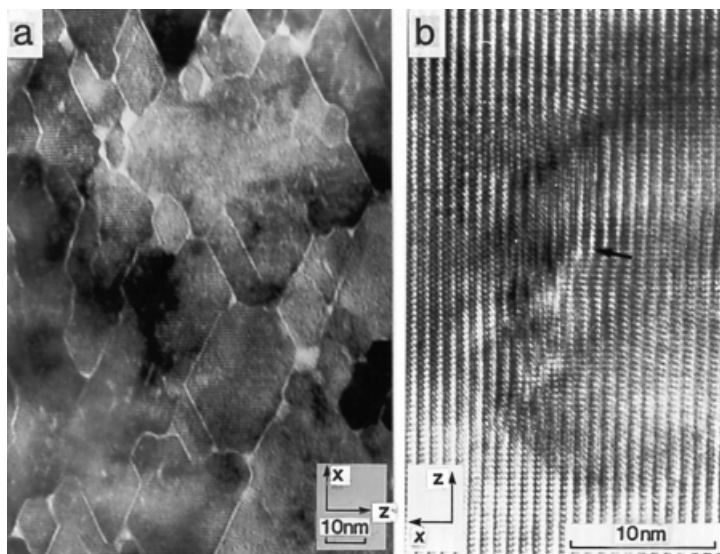


Fig. 4.6 High resolution electron micrograph of natural goethite: a) Diamond-shaped cross sections of domains running along [010] and bounded by {101} faces. Lattice fringes correspond to the *a*-parameter. b) Higher magnification shows the *a* fringes (ca. 1 nm) and structural distortions. (Smith & Eggleton, 1983; with permission; courtesy R.A. Eggleton).

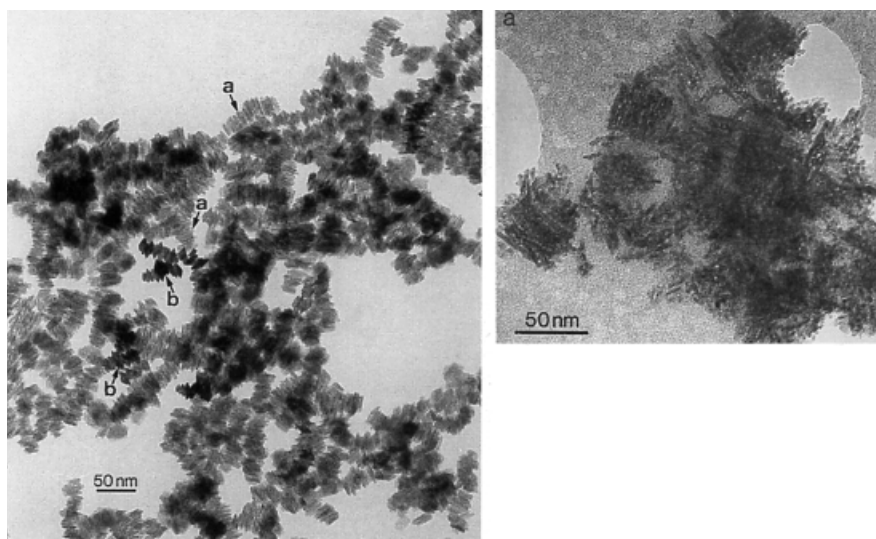


Fig. 4.7 Left: Goethite grown from a partially neutralized $\text{Fe}(\text{NO}_3)_3$ solution (initial pH 1.7). The small needles of the rafts lie with their needle axis either parallel (a) or perpendicular (b) to the plane of the paper. In the latter case, the dia-

mond-shaped cross section indicates that the needles are embraced by {101} faces (courtesy S. Glasauer). Right: Goethite produced by oxidation of a Fe^{II} solution at 25 °C and pH 6–7.

high. Differential interference contrast and AFM showed growth hillocks elongated along [100] with rounded macrosteps and much narrower steps on the growth (100) surfaces of natural goethite crystals (Rakovan et al., 1999). The corresponding cleavage surfaces showed atomically flat terraces separated by steps of 0.9 nm and multiples of this value. AFM (Plate 4.I) showed that a large, synthetic goethite crystal had well developed {011} lateral faces and stepped (010) faces on the top. The steps are bounded by vicinal {102} faces with the step heights being between 10 and 250 nm; smaller steps (~1 nm) also occur on the (010) face itself (Weidler et al. 1996). It seems as if (010) faces are a feature of the larger crystals with more well developed faces; such crystals also display a greater variety of faces. AFM examination showed no evidence of spiral dislocations on goethite crystals (Weidler et al. 1996).

In summary, although other forms cannot be excluded, it appears that the {011} and {102} forms are the most important ones particularly for synthetic goethites. They will, therefore, determine the configuration and density of surface functional Fe-OH groups which participate in adsorption reactions (see Chap. 11).

Goethite crystals produced by *oxidation of Fe^{II} solutions* at ambient temperature in neutral solution (Fig. 4.7; right) – a process likely to occur in nature – are usually much less developed and the crystals are smaller ($MCL_b \approx 10$ nm) than those obtained in alkaline Fe^{III} solutions. If Al is taken up in the structure, these crystals become extremely small ($MCL_a \sim 5$ nm) and show almost no particular habit. At higher pH (~12) the crystals are again acicular ($MCL_a \sim 30$ nm) despite containing structural Al ($Al/(Al+Fe) \sim 0.3$); they show internal disorder, however, and stars are frequent. This morphology is also observed for soil goethites (see Chap. 16).

Goethite precipitated from *acidic Fe^{III} solutions* may be acicular, rod-like (Van der Woude et al., 1984) or cubic (Van der Woude & De Bruyn, 1984). The dimensions of the latter crystals are below 100 nm. In cross section, the rod-like crystals had a diamond shape with an axial angle of 47° and were enclosed by (100) and (201) planes. HRTEM showed that while the crystals were crystallographically homogeneous, they contained interior spaces up to one nm across. Although it has been suggested that such spaces might be indicative of a substructure (Van der Woude et al., 1984), examination of TEMs of the sectioned crystals indicates that nothing more than domains are present. The different morphologies are considered to reflect differences in pH, (OH/Fe ratio) and in temperature during formation (Van der Woude & De Bruyn, 1984). Under conditions of high ionic strength (0.2 M), these small acicular goethites flocculate in acid media to form rafts of parallel rods (Atkinson et al., 1968; Murphy et al., 1976; Van der Woude et al., 1984; Koch et al., 1986) (see Fig. 4.7; left).

4.2.1.2 Domainic character

Goethite crystals, particularly those grown in alkaline media, frequently consist of parallel subunits, the so-called domains or intergrowths. These domains extend along the *a*-axis and are stacked along the *b*- and *c*-axes. Owing to the unequal lengths of the domains, multidomainic crystals often display irregular ends with a series of well-developed (210) faces (Fig. 4.3) (Cornell et al., 1974; Schwertmann et al., 1985; Koch et al., 1986; Cornell & Giovanoli, 1986). Individual domains are between 10 and 30 nm wide.

When crystallite size is estimated from XRD line broadening using the Scherrer formula, multidomainic crystals appear to have a lower width (in the *b*- and *c*-direction) than that obtained by direct measurement from electron micrographs. This is because the mean crystallite lengths in these directions (MCL) obtained from XRD line broadening, reflect domain size which is, of course, smaller than that of the crystal. As the number of domains per crystal decreases, MCL and the overall needle width approach each other until, when the crystals are monodomainic, they agree. A systematic reduction in the number of domains can be achieved by incorporation of increasing amounts of Al in the crystal structure (Schulze & Schwertmann, 1984).

TEM studies showed that the domains appear to nucleate somewhere in the centre of the crystal during the early stages of crystal formation (Cornell & Giovanoli, 1986). Nucleation can take place in both the [100] and [001] directions, but subsequent growth is along [100]. Multidomainic crystals of goethite arise as a result of interference in the alignment of surface nuclei. Each intergrowth appears to be slightly misoriented with respect to its neighbours. In general, the divergence between domains does not appear to be more than a few hundredths of a degree. HRTEM of the region across the domain boundaries showed that the domains are extremely coherent with no localized atomic disorder along the boundary (Fig. 4.8) (Cornell et al., 1983). The slight divergence between the domains appears to be taken up by widely spaced dislocations. The presence of these dislocations can account for the formation of holes in or through the crystals as a result of proton attack (Cornell et al., 1974; Schwertmann, 1984a) (see Chap. 12). Dislocations are regions of more active coordination sites and are also associated with an excess energy emanating from structural disorder in the vicinity; they are, thus, sites of preferential acid attack. As the dislocations pass right through the crystal, acid attack at these sites readily leads to hole formation.

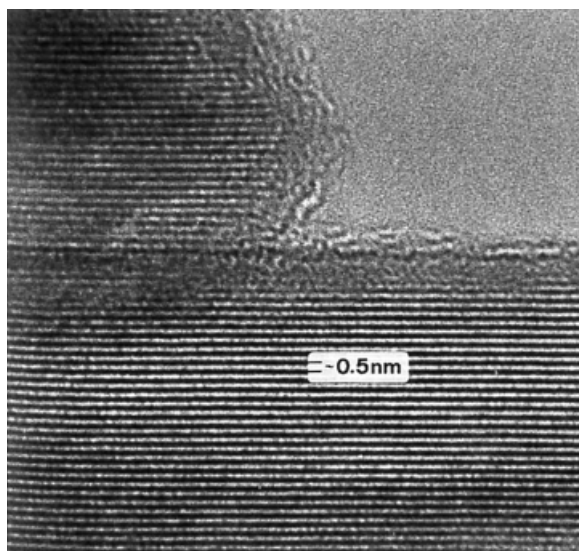


Fig. 4.8 High resolution electron micrograph of two goethite domains and their interdomainic zone. The lattice fringes at 0.5 nm correspond to the (200) spacing (courtesy S. Mann, Bristol).

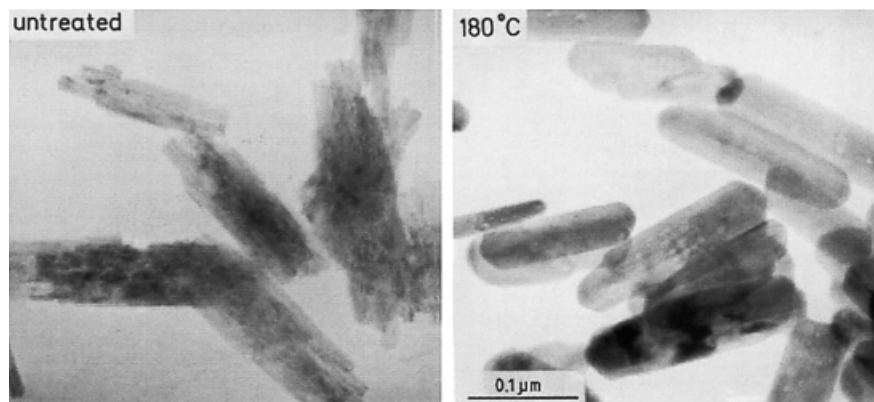


Fig. 4.9 Crystal healing of goethite: polydomainic serrated goethite crystals formed at 4 °C transformed to monodomainic smooth crystals after hydrothermal treatment at 180 °C (Schwertmann et al., 1985, with permission).

Conditions which promote multi-domainic goethites are high ionic strength (either [KOH] or salt) and also low synthesis temperature (<40 °C). In alkaline solutions, multi-domainic character decreases and domain width increases as Al substitution increases to $\text{Al}/(\text{Fe}+\text{Al})$ of 0.15, whereas at $\text{Al}/(\text{Al}+\text{Fe}) > 0.15$ single domain crystals result (Schulze & Schwertmann, 1984; Mann et al., 1985). Multidomainic goethites can recrystallize to single domain crystals as a result of hydrothermal treatment at 125–180 °C (Fig. 4.9) (Schwertmann et al., 1985).

4.2.1.3 Twinning

Goethite twins on the (210) plane. Twinned crystals display a great variety of shapes but are basically either composite or epitaxial. Composite goethite twins may have one or more branches (Fig. 4.10; upper left) (and are sometimes termed dendritic) or be “star-shaped” (Fig. 4.10; upper right). The latter are fully developed composites with a pseudo-hexagonal symmetry, i.e. mimetic twins. They give rise to a [001] zone electron diffraction pattern. A HRTEM study of branched crystals imaged the lattice spacings of the (210) twin plane and the (200) spacings parallel to the needle axis (Maeda & Hirono, 1981). The measured angle between the main crystal and its branch was ca. 117°, in good agreement with the calculated value of 117.5° for the angle between (200) and (210). As this value is less than 120°, the outgrowth has both a coherent and an incoherent boundary with the parent crystal (Fig. 4.10). Branched twinning is undesirable because it renders maghemite prepared from goethite less suitable for use in magnetic recording devices. The presence of carbonate ions reduces branched twinning of goethite crystals formed in Fe^{II} systems (Kiyama et al., 1986).

Epitaxial twins (Fig. 4.11) consist of a hematite centre with outgrowths of acicular goethite. As the structures of both goethite and hematite are based on an hcp anion array, some of the interplanar spacings in the two compounds are similar and this fa-

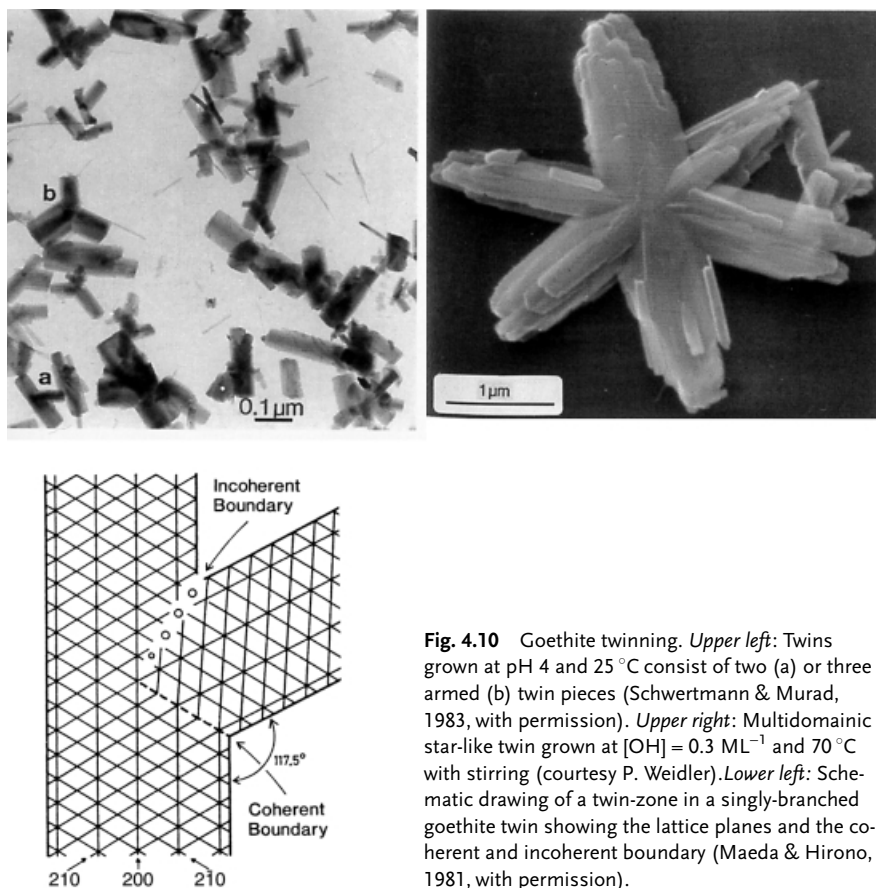


Fig. 4.10 Goethite twinning. *Upper left*: Twins grown at pH 4 and 25 °C consist of two (a) or three armed (b) twin pieces (Schwertmann & Murad, 1983, with permission). *Upper right*: Multidomainic star-like twin grown at $[\text{OH}] = 0.3 \text{ ML}^{-1}$ and 70 °C with stirring (courtesy P. Weidler). *Lower left*: Schematic drawing of a twin-zone in a singly-branched goethite twin showing the lattice planes and the coherent and incoherent boundary (Maeda & Hirono, 1981, with permission).

cilitates epitaxy. The $\{100\}$ planes of hematite act as a substrate for goethite growth ($d_{(200)(\text{Gt})} = 0.151 \text{ nm}$ and $d_{(300)(\text{Hm})} = 0.145 \text{ nm}$). Each goethite outgrowth develops in the $[100]$ direction with the (210) plane of goethite almost parallel to the hematite a -axis and the (001) plane of goethite parallel to the (001) hematite basal plane (Atkinson et al., 1968, Barron et al. 1997).

Nucleation of twinned goethites appears, in contrast to formation of acicular crystals, to occur within the ferrihydrite aggregates and to be confined to the early stages of the precipitation reaction. The presence of different types of twins in a sample can be correlated with synthesis conditions, i.e. pH, temperature, ionic strength, $[\text{Fe}^{3+}]$ and the presence of interfering species (Cornell & Giovanoli, 1985). Epitaxial twins occur in goethites grown from ferrihydrite in both acid (Hsu & Wang, 1980) and alkaline media, whereas star-shaped twins are produced only at high pH. Branched twins can be obtained over the whole pH range and from both Fe^{II} and Fe^{III} precursors. Very rapid preferential growth along the needle axis e.g. at high $[\text{OH}]$, appears to inhibit twinning.

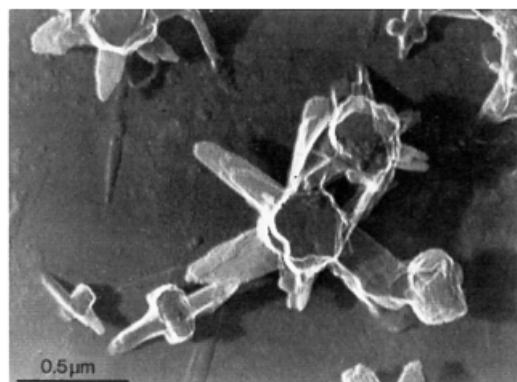
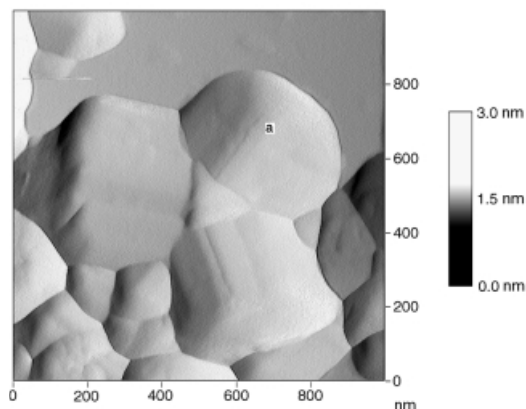


Fig. 4.11 Replica (upper) and scanning force electron micrograph (lower) of goethite grown epitaxially on hematite cores (upper: see Cornell, 1985; lower: Barron et al. 1997, with permission).



4.2.1.4 Effect of additives

Additives usually alter only the length-to-width or width-to-thickness ratio of the acicular crystals. Growth of long, thin crystals (aspect ratio >12) is induced by high levels (>0.1) of Mn or Co and is attributed to adsorption rather than substitution. These ions have the same influence on aspect ratio whether goethite is grown from Fe^{II} or Fe^{III} systems and over the pH range 7–13.

Incorporation of Al makes the acicular crystals shorter and, at the same time, broader (in terms of MCL_a) and thicker (MCL_c) and also less domainic (see Chap. 3, Fig. 3.4). High enough levels of silicate species strongly modify the morphology of goethite grown from ferrihydrite, akaganéite and lepidocrocite at pH 12. With increasing concentration of these species, the morphology changes to broad acicular crystals through to apparent pseudohexagons and finally to bipyramids (Fig. 4.12) (Cornell et al., 1987; Cornell & Giovanoli, 1987a, 1990). The alteration in morphology has been attributed to preferential adsorption of silicate species on the terminal (210) planes of the crystals; adsorption retards growth and so enhances the development of these planes at the expense of (101) planes. Silicate did not alter goethite morphology in acid or neutral media.

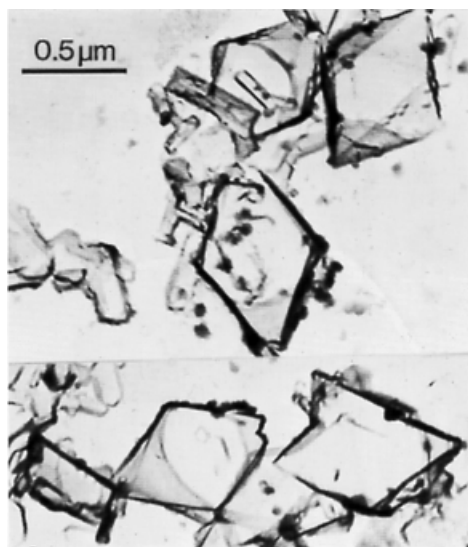


Fig. 4.12 Replica of bipyramidal goethite crystals grown at $[\text{Si}] = 10^{-3} \text{ M}$, pH 12 and 70°C (Cornell & Giovanoli, 1987a; with permission).

Sucrose (at sucrose/Fe = 0.01) led to development of wedge-shaped goethite outgrowths on hematite centres due possibly to temporary adsorption of sucrose at the ends of the crystals (Cornell, 1985). Monodisperse suspensions of subrounded crystals of goethite < 100 nm across have been produced by interaction of high levels of cysteine with ferrihydrite (cysteine/Fe = 1.0) at pH 7–8 (Cornell et al., 1991). Acicular crystals up to 1 μm in length and radially grouped into aggregates have been grown hydrothermally by oxidation of Fe^{2+} in a Na acetate-hydroxyl amine solution (Ardizzone & Formaro, 1985) and in a slightly acid solution with amino-alkyl silicate (Bye & Howard, 1971).

Many additives which do not modify crystal morphology to any extent lead to development of pits and surface irregularities on the goethite surface (Cornell & Giovanoli, 1987). Foreign species can also promote twinning of goethite. Mn promoted branched twins (Cornell & Giovanoli, 1987) and maltose, glucose and citrate led to epitaxial twins consisting of two or three outgrowths of goethite projecting from opposite, prismatic faces of an elongated crystal of hematite (Schwertmann et al., 1968; Cornell, 1985); the organic species modified the morphology of the hematite centre.

4.2.2

Lepidocrocite

The basic morphologies of lepidocrocite are lath-like or tabular. No example of twinning has been reported. Macrocrystalline lepidocrocite in the form of tabular crystals has $\{010\}$ as the predominant form (Fig. 4.13). Other massive varieties of lepidocrocite include micaceous and fibrous textures and aggregated scales.

Synthetic crystals of lepidocrocite are platy or lath-like, elongated in the a -direction and terminate in $\{101\}$ faces. The predominant face is $\{010\}$ and crystals often lie on this face. Lepidocrocite is commonly formed by oxidation of Fe^{II} systems. The crystal

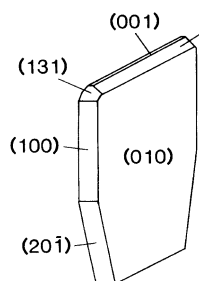


Fig. 4.13 Crystal forms of lepidocrocite (Ramdohr & Strunz, 1978, with permission).

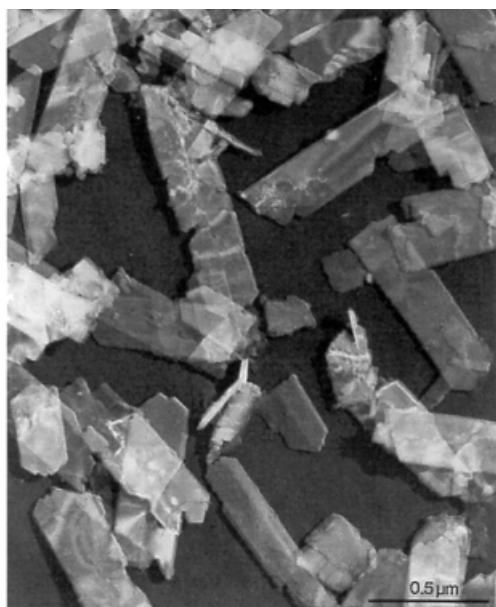
habit varies with the conditions under which oxidation takes place. With slow crystallization (= oxidation) and/or higher temperatures, single, well developed laths form (Schwertmann & Taylor, 1972a; Giovanoli & Brüttsch, 1975; Gomez-Villacieros et al., 1984). Such crystals are 0.5–1.0 μm long, 0.1–0.2 μm wide and <0.1 μm thick (Fig. 4.14a). If formed at a somewhat faster rate, the crystals are thinner and multi-domainic (Schwertmann & Thalmann, 1976). The domains are ca. 10–20 nm wide and, like single domainic crystals, terminate in $\{101\}$ faces. They project from a non-domainic, central region of the crystal and are separated by free space (Fig. 4.14b). Under conditions of very rapid oxidation at low pH (i.e. high driving force for crystallization) and/or in the presence of crystallization inhibitors, grassy type or “hedgehog-like” spherulites form (Fig. 4.14c). Examples of inhibitors are silicate (Schwertmann & Thalmann, 1976), organics (Brauer, 1982) and Al (Schwertmann & Wolska, 1990). Such crystals are small and, when single, may lie on the a - c plane and exhibit (010) lattice fringes of ca. 1 nm (Fig. 4.14d). Rapidly precipitated lepidocrocite can also grow as thin, crumpled sheets (Mackenzie & Meldau, 1959; Fryer, 1982). In the presence of silicate (e.g. 0.33 M) and at 80 °C in M KOH, lepidocrocite recrystallizes to diamond-shaped or rectangular particles (Fig. 4.14e) (Schwertmann & Taylor, 1972; Cornell & Giovanoli, 1990) with sharper X-ray lines, a smaller surface area and modified Mössbauer parameters (Murad & Schwertmann, 1984). The presence of Zn induced lepidocrocite to form isometric crystals (Domingo et al., 1994).

4.2.3

Akaganéite and schwertmannite

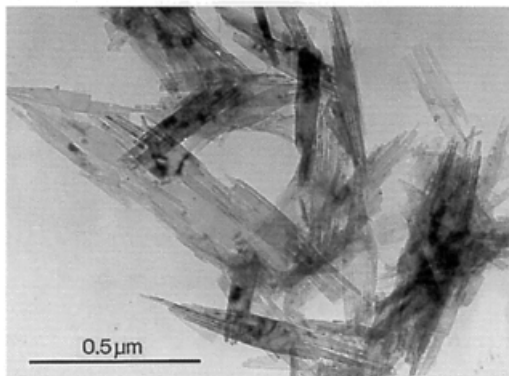
Akaganéite displays two basic morphologies, somatoids (spindles) and rods (Fig. 4.15), both types having a fairly narrow size distribution. Crystal lengths are rarely greater than 0.5 μm . Akaganéite from the vicinity of the Akagané mine in Japan consists of lath-like crystals elongated along $[001]$ and ca. 0.25 μm in length (Mackay, 1962). Spindle-shaped akaganéites found in Red Sea brine sediments were 0.1–0.5 μm long and had fibrous ends (see Fig. 15.8c) (Holm et al., 1983). Macrocrystals of akaganéite have not been found in nature.

Akaganéite formed by hydrolysis of acid FeCl_3 solutions ($\text{OH}/\text{Fe} = 0$) at 25–100 °C precipitates as somatoids between 0.2–0.5 μm in length and 0.02–0.1 μm in width (Fig. 4.15a). The crystals are elongated along the c -axis and are bounded by (001) and (200) planes (Mackay, 1962). Crystals grown at room temperature display a square

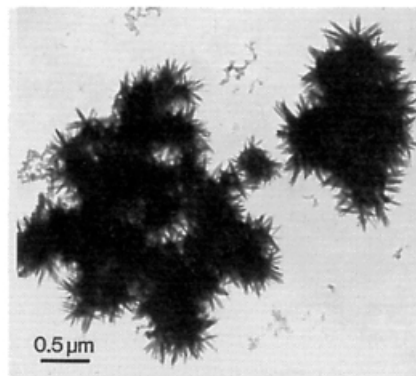


a

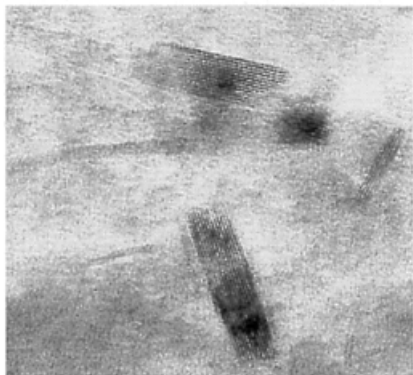
Fig. 4.14 Synthetic lepidocrocite produced by oxidation of a FeCl_2 solution. a) Monodomainic, lath-shaped crystals, produced by oxidation with $100 \text{ mL air min}^{-1}$ at 50°C and pH 7.5 shadowed with 5 nm chromium at 45° (Courtesy R. Giovanoli). b) Multidomainic crystals obtained at pH 7–7.5 and room temperature (see Schwertmann & Taylor, 1972a). c) Crystal aggregates produced in the presence of urotropin (courtesy R. Giovanoli). d) Very small crystals showing (010) lattice fringes of $\sim 1 \text{ nm}$ (Schwertmann & Taylor, 1979, with permission). e) Cubic crystals formed after ageing multidomainic crystals shown in (b) in $M \text{ KOH}$ containing $3.32 \cdot 10^{-3} M \text{ Si}$ at 80°C for 1749 h (Schwertmann & Taylor, 1972, with permission).



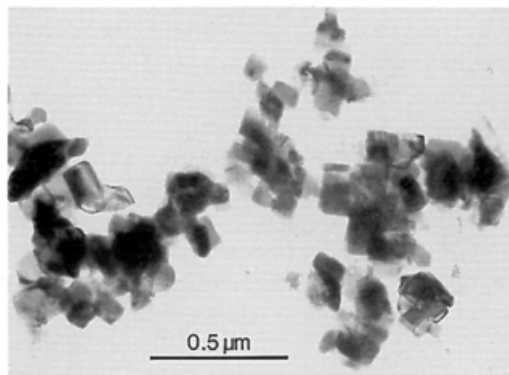
b



c



d



e

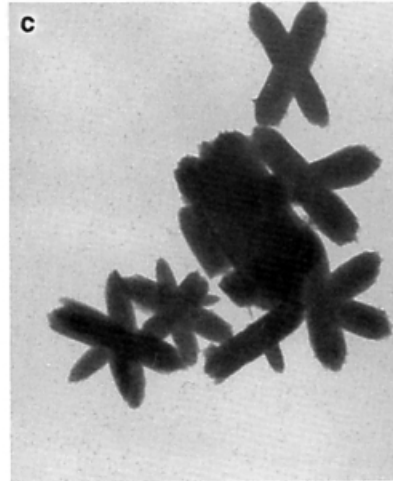


Fig. 4.15 Synthetic akaganéite a) somatoid (Murad, 1979, with permission) (b) rod-like, (c) Si-akaganeite (Schwertmann & Cornell, 2000, with permission)

cross section, whereas those grown at higher temperatures are circular (Mackay, 1962). The differences in cross section have been attributed to differences in the rates of growth – months versus days. HRTEM showed that internally the crystals are crystallographically homogeneous, but possess stepped edges bounded by (200) planes (Galbraith et al., 1979). Striations that develop on the surfaces of the crystals during TEM examination are the result of electron beam damage and do not indicate the presence of a substructure (Fryer, 1979).

Somatoids are often twinned on the (322) plane to give star-shaped or x-shaped twins (Fig. 4.15 a). Incorporation of low levels of Si in the structure promotes twinning; with 0.04 mol mol⁻¹ Si, akaganéite was almost 100% twinned (Cornell, 1992). These crystals have a visibly roughened surface. Increasing citrate concentration during forced hydrolysis at 100 °C and pH 1 reduced the length of the somatoids from 0.6 µm in the absence of citrate to some tens of nm at a citrate/Fe ratio of 0.02; a similar reduction in size was observed for goethite crystals (Kandori et al. 1991).

Rod-like crystals (Fig. 4.15 b) are formed from partly neutralized Fe^{III} solutions (0 < OH/Fe < 3) (Mackay, 1962; Atkinson et al., 1977; Paterson & Tait, 1977). They are usually monodisperse, around 50 nm long, 6 nm wide and also elongated in the [010] direction. In concentrated suspensions, these rods associate to form tactoids, i.e. spindle-shaped, anisotropic liquid droplets (0.2 mm long) of spontaneously orientated particles (Zocher, 1925; Mackay, 1962).

Akaganéite formed in air by solid state transformation from FeCl₂ · 4 H₂O exists as sheets of long, thin, lathlike crystals (Mackay, 1962). Wolf et al. (1967) reported that akaganéite produced by boiling 0.3 M FeCl₃ for 5 hr recrystallized over 2.5 years at RT to give prism-shaped crystals. Nightingale and Benck (1960) claimed to have produced large (mm), hexagonal plates of akaganéite by boiling a Fe^{III} solution with urea in the presence of dihydroxyethylene glycol. Reeves and Mann (1991) showed a TEM of a rosette-like, polycrystalline aggregate of akaganéite, 1–2.5 µm wide, produced by forced hydrolysis of FeCl₃ in the presence of 1–2 ethylene diphosphonic acid. These few reports suggest that suitable organic ligands may induce further novel morphologies of akaganéite crystals. Uniform, capsule-shaped particles of akaganéite ca. 0.2 µm long and 0.05 µm wide were obtained in the presence of F⁻ ions (F/Fe = 1) (Fig. 4.15 c). The composition is FeO(OH)_{0.7}F_{0.3} · 0.3 H₂O (Naono et al., 1993).

Natural and synthetic *schwertmannite* forms perfectly spherical, hedge-hog-like, crystal aggregates several µm in size (Fig. 4.16; upper). They consist of radially oriented, filamentous crystals, ca. 100nm long and 10nm wide (Fig. 4.16, lower), and elongated along the *c*-axis (Bigham et al., 1990; Bigham & Nordstrom, 2000; Gagliano et al. 2002).

4.2.4

Ferrihydrite

Highly-broadened XRD peaks and electron diffraction patterns indicate that ferrihydrites are characterized by small crystal size and/or low structural order. TEM shows single spherical particles, ca. 4–6 nm in size (Fig. 4.17). At higher magnification (HRTEM), 6-line ferrihydrite appeared as single crystals with a hexagonal outline and

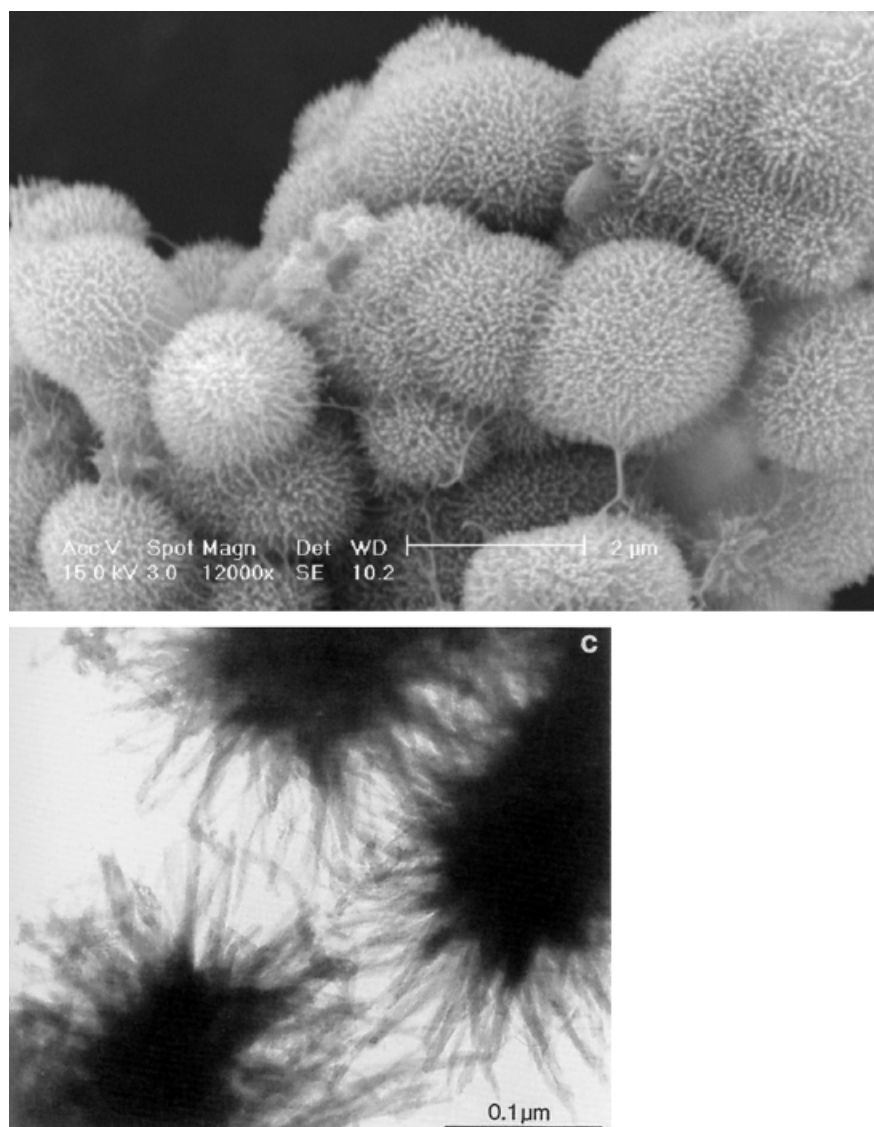


Fig. 4.16 Upper: SEM micrograph of crystal aggregates of schwertmannite from a mine drainage wetland (Gagliano et al. 2003, with permission): Lower: TEM micrograph of schwertmannite (Bigham et al., 1990; with permission).

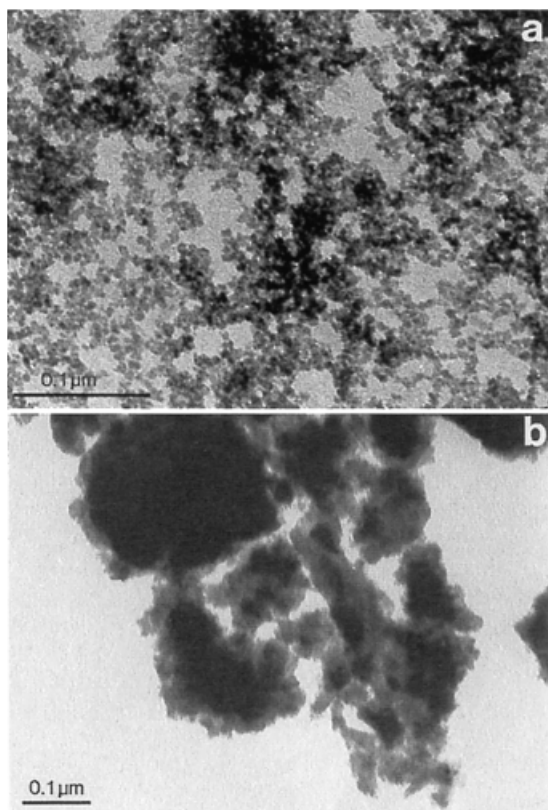


Fig. 4.17 TEM of (a) 6-line ferrihydrite produced by a 12 min acid hydrolysis of $\text{Fe}(\text{NO}_3)_3$ at 75 °C and (b) a 2-line ferrihydrite formed by fast hydrolysis of Fe^{III} solution at RT under neutral conditions (Schwertmann & Cornell, 2000; with permission).



Fig. 4.18 HRTEM of 6-line ferrihydrite with lattice images showing its crystalline nature (Janney et al. 2000 a, with permission courtesy D. E. Janney).

appreciable internal order as seen from lattice fringes (Fig. 4.18), whereas both of these features are less well expressed in the 2-line variety (Janney et al. 2000a). XRD shows that a continuous series between 2- and 6-line ferrihydrite, with respect to crystallinity, exists *in vitro* (Schwertmann et al. 1999; Schwertmann & Cornell, 2000) as well as *in situ* (Carlson & Schwertmann, 1981).

4.2.5

Hematite

The commonest habits for hematite crystals are rhombohedral, platy and rounded (Fig. 4.19). The plates vary in thickness and can be round, hexagonal or of irregular shape. Under hydrothermal conditions, these three morphologies predominate successively as the temperature decreases (Rösler, 1983). The principal forms are given in Table 4.1. Hematite twins on the {001} and the {102} planes. The crystal structure of hematite has a less directional effect on crystal habit than does that of goethite and for this reason, the habit of hematite is readily modified. A variety of morphologies has been synthesized, but in most cases, the crystal faces that enclose the crystals have not been identified.

Efforts aimed ultimately at tailoring well defined morphologies have been directed towards calculating the equilibrium morphology of hematite (Mackrodt et al., 1987; Mackrodt, 1988; Reeves & Mann, 1991; Rohl & Gay, 1996). The method involves using an atomistic simulation technique with empirical potentials to calculate the energies of selected surface planes¹⁾ and hence the morphology with minimum surface area. The calculated surface energies for a number of low index planes are listed in Table 4.3. Different authors obtained different values (Mackrodt, 1988; Reeves & Mann, 1991), but there is some agreement, based on these calculations, that the rhombohedral plane {012} should frequently occur – and in fact it does. In view of the predominance of platy crystals, the lower value of the listed surface energies for the {001} plane in Table 4.3 appears to be the more acceptable. Possibly because the surface energies of the various low index faces are fairly similar, the order of stability of these faces may be altered quite easily by preferential adsorption of ionic species or by slight alterations in reaction conditions.

Macrocrystalline hematite can be rhombohedral, platy or fibrous. Crystals formed from solution are thick plates or rhombohedra, whereas those grown from the vapour phase form thin plates (Sunagawa, 1987a). An example of the latter are the large, specular crystals from the island of Elba which probably formed by reaction of gaseous FeCl_3 with water vapour. The platy crystals with predominant {001} faces are termed micaceous (Fig. 4.19) or specularite; they are sometimes aggregated to form rosettes (“iron roses”). Martitic hematite appears as octahedra or dodecahedra formed by pseudomorphic transitions²⁾ from magnetite and pyrite, respectively. He-

1) The calculations usually assume relaxed surfaces. Unrelaxed surfaces (i.e. those with the same properties as the bulk crystal) lead to surface energies which are too high by a factor of

ca. 2 and produce a calculated morphology different from any that is actually observed.

2) A pseudomorph has the habit of the original substance and this may not in any way reflect the structure of the actual crystal.

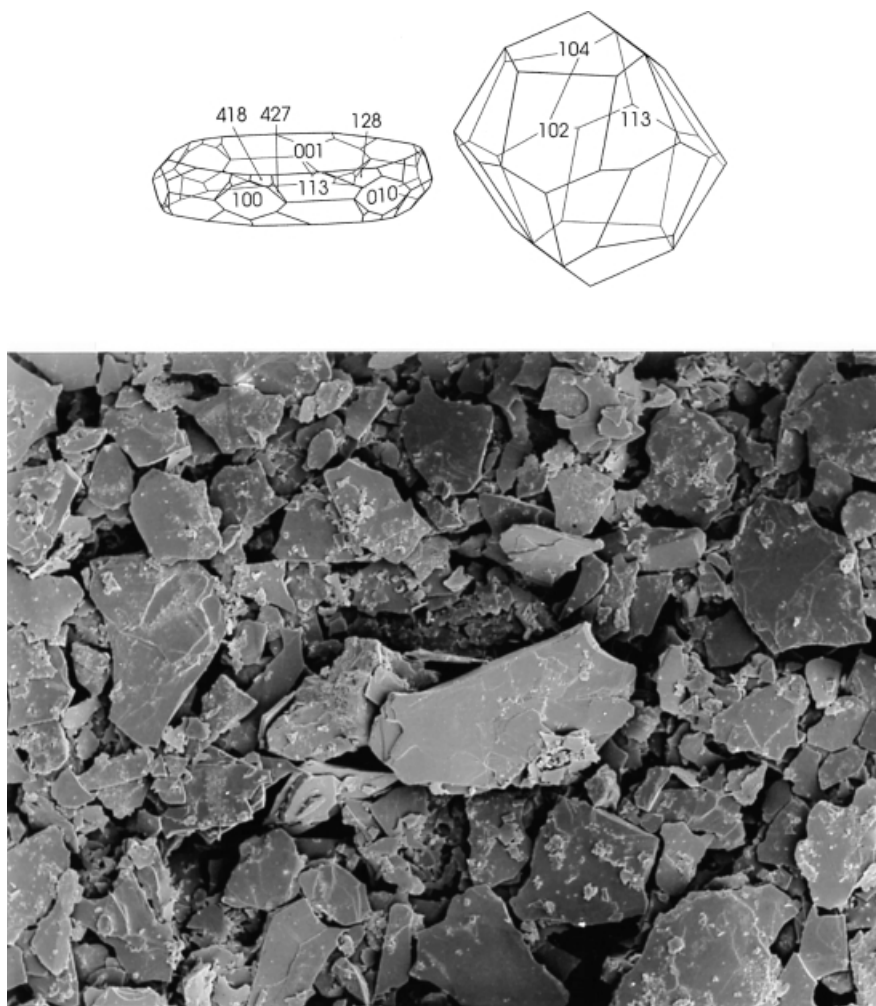


Fig. 4.19 Upper: Crystal forms of platy and rhombohedral hematite (Courtesy H. Stanjek). Lower: Micaceous hematite from Western Australia (Courtesy R. Giovanoli, magnification 250x).

matitic ores can be massive, oolitic, specular or botryoidal with a radial fibrous texture. Sunagawa (1961, 1962) studied the surface topography and growth mechanism of natural crystals of platy hematite: the (001) faces often show spiral dislocations.

Morphologies of synthetic hematite include plates and discs, rods, spindles, spheres, ellipsoids, double ellipsoids, rhombohedra, stars, cubes and peanuts. In the absence of additives, hexagonal plates, which are often rounded, and rhombohedra predominate. Each morphology can be obtained by more than one synthesis route. Two common ways of producing idiomorphic hematite crystals in aqueous systems

Tab. 4.3 Calculated energies for relaxed, low index surfaces of hematite

Plane		Surface energy/J m ⁻²	
		M ¹⁾	R & M ²⁾
001	basal	1.53	2.31
100	prismatic	2.36	2.25
102	rhombohedral	1.47	1.96
110	prismatic	2.03	–
101		2.41	2.84
120		–	2.33
104		–	2.64

1) Mackrodt (1988, with permission)

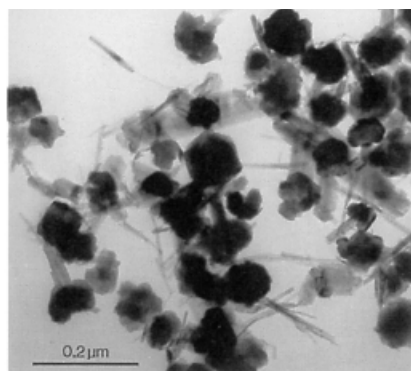
2) Reeves & Mann (1991, with permission)

are via ferrihydrite in weakly acid to alkaline media and by the hydrolysis of Fe^{III} salt solutions at low pH and at elevated temperature, the so-called “forced hydrolysis method”.

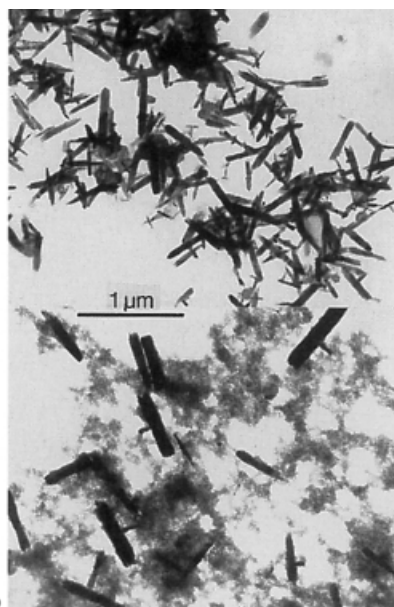
Hematite grown from ferrihydrite in the absence of additives at temperatures <100 °C in aqueous systems i.e. at a pH where the solubility product of ferrihydrite is exceeded, forms hexagonal or subrounded plates with {001} as the predominant form (Fig. 4.20a). The platy nature of these crystals can also be recognized from differential X-ray line broadening with hk0 lines (110, 300) being sharper than hkl lines (104, 012, 113). This indicates better crystal development in the *a*- than in the *c*-direction. The plate diameter ranges from <100 nm at pH 8 to 1–5 µm in 5 M [OH] (Cornell & Giovanoli, 1985; Torrent & Schwertmann, 1987) and increases with increasing temperature.

Additives, such as citrate or maltose (ligand/Fe = 0.0001–0.001, pH 10–12) cause hematite to grow preferentially along [001] and form rods, often with fibrous ends (Fig. 4.20b) (Schwertmann et al., 1968; Cornell & Schwertmann, 1979; Cornell, 1985; Reeves & Mann, 1991). The rodlike morphology appears to be caused by preferential adsorption of foreign species on the {110} or {104} planes. Oxalate (oxalate/Fe = 0.001, pH 6–7; 60 °C; Fischer & Schwertmann, 1975), caused hematite to grow as granular, polydomainic ellipsoids (Fig. 4.20c). Similar ellipsoids form in the presence of silicate (Si/Fe = 0.001; pH 12; Cornell et al. 1987) and phosphate at pH 9 (Galvez et al. 1999) and these crystals show outgrowths of goethite. In the presence of phosphate, ellipsoidal hematite forms over the pH range 1–9; the crystals formed by forced hydrolysis are narrow, spindle-like ellipsoids, whereas those formed from ferrihydrite are thicker and lens-like.

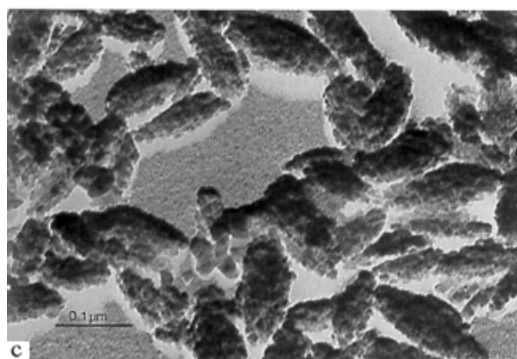
Aluminium in the ferrihydrite system not only suppresses goethite in favour of hematite (see chap. 14) but also affects the morphology of hematite, probably by entering the structure. At temperatures of between 70 and 150 °C, a shift was noticed from rhombohedra to plates whose diameter and thickness were at a maximum at an Al/(Fe+Al) ratio of 0.05 (Schwertmann et al., 1979; Barrón et al., 1984; Barrón & Torrent, 1984; Wolska & Szajda, 1987). At higher levels of substitution, the plates became extremely thin and structural strain increased (Stanjek & Schwertmann, 1992)



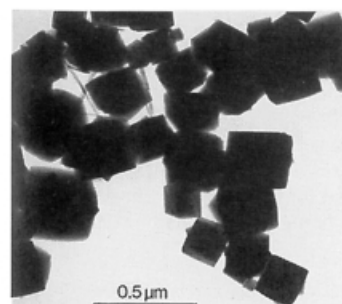
a



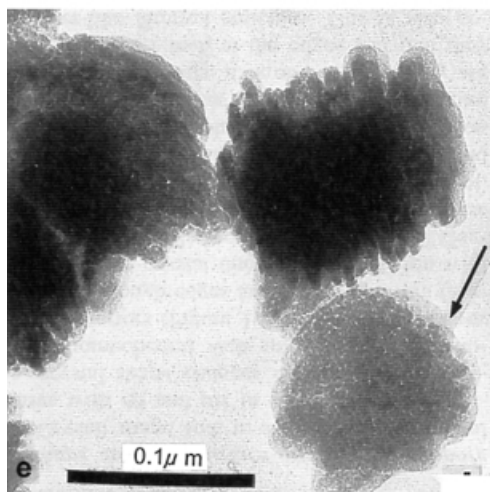
b



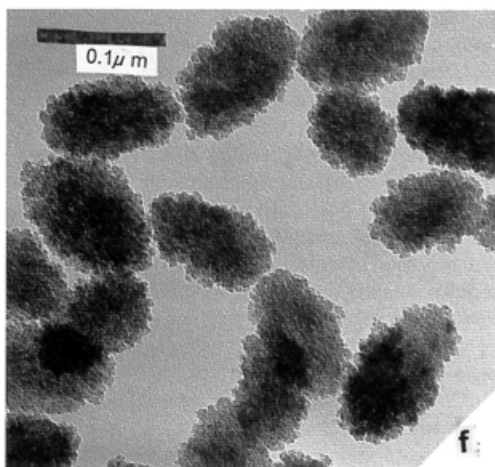
c



d



e



f

indicating that growth in the *c*-direction is inhibited by Al substitution (Schwertmann et al., 1979).

Al-hematites formed slowly from Al-ferrihydrite at 25 °C over ~20 years, varied between rhombohedra at low substitution and multidomainic ellipsoids ca. 100 nm across with a grainy interior at higher substitution ($\text{Al}/(\text{Al}+\text{Fe}) = 0.15$) (Fig. 4.20 e & f) (Schwertmann et al. 2000). Allophane as a source of Al had the same effect (Schwertmann et al. 2000 a). *Mn substituted* hematites grown from ferrihydrite were ellipsoidal in the presence of oxalate and platy in the presence of NaHCO_3 buffer (Cornell & Giovanoli, 1987; Cornell et al., 1990). *Cu substituted* ($0.09 \text{ mol mol}^{-1}$) hematite grows as large ($0.2 \mu\text{m}$) rhombohedral crystals; the crystal faces are most probably {102} or {104} (Fig. 4.20 d) (Cornell & Giovanoli, 1988).

Hematites grown by *forced hydrolysis* of acidic Fe^{III} solutions at elevated temperatures also show a range of crystal morphologies. The type of anion, the acidity and the presence of additives appear to be main factors that influence the shape (Matijevic & Scheiner, 1978; Kandori et al., 1991; Bailey et al., 1993). Additives appear to act by adsorbing on specific planes of the growing crystal. At close to 100 °C, rhombohedral crystals, 50–100 nm in size, sometimes showing intergrowths (stepped appearance) (Fig. 4.21 a, b) formed from nitrate and perchlorate ($0.001\text{--}0.2 \text{ M}$), whereas sub-rounded plates grew from chloride solutions (Fig. 4.21 c). In the presence of phosphate, spindle-like ellipsoids, elongated along the *c*-axis were obtained (Ozaki et al., 1984; Reeves & Mann, 1991). The spindles had rough, poorly defined surfaces which were considered to be composed of first, second and third order prismatic faces stabilized by adsorbed phosphate. The Fe-Fe spacing of 0.27 nm on these prismatic faces (see Fig. 10.3) is suitable for bidentate coordination of the phosphate and oxalate ions at the surface. Electron diffraction and HRTEM examination showed that hematite crystals formed from FeCl_3 solutions were bounded by {104} planes and those from $\text{Fe}(\text{ClO}_4)_3$ solutions by {102} planes (Reeves & Mann, 1991). Bailey et al. (1993) used TEM on dried samples and also on frozen liquid films (Cryo-TEM) to monitor precipitation of hematite from heated FeCl_3 solutions with different $[\text{Fe}^{\text{III}}]$ and acidities. In some cases, hematite appeared to nucleate on the akaganéite rods (which formed first) and it was suggested that the concentrations of the starting reagents influenced crystal morphology (spheres, cubes or double ellipsoids) by influencing the aggregation behaviour of the akaganéite. Uniform, cubic crystals were formed by forced hydrolysis of FeCl_3 in ethanol/water and ellipsoidal crystals in ethylene glycol/water solutions (Hamada & Matijevic, 1982; Matijevic & Cimas, 1987). Hamada and Matijevic (1982) discussed the morphology of hematite obtained in mixed solvent systems in terms of

◀ **Fig. 4.20** Synthetic hematites grown from ferrihydrite at temperatures < 100 °C (Schwertmann, unpubl.) a) Hexagonal plates grown at pH 7 and RT; acicular crystals are goethite; b) Laths grown at pH 11 and 80 °C in the presence of $2.5 \cdot 10^{-3} \text{ M}$ citrate (see Schwertmann et al., 1968). The fine granular material is unreacted ferrihydrite; c) Framboids grown at pH 6 and 70 °C in the presence of $2 \cdot 10^{-2} \text{ M}$ oxalate (see Fischer & Schwertmann, 1975, with permission); d) Cubes grown at pH 12.2 and 70 °C in the presence of Cu ($\text{Cu}/(\text{Fe}+\text{Cu}) = 0.09$) (see Cornell & Giovanoli, 1988); e) & f) Polydomainic crystals grown from Al ferrihydrite ($\text{Al}/(\text{Al} + \text{Fe} = 0.15)$) after 16–20 years at 25 °C and pH 4 (e) and pH 5 (f) (Schwertmann et al. 2000, The Clay Minerals Society; with permission).

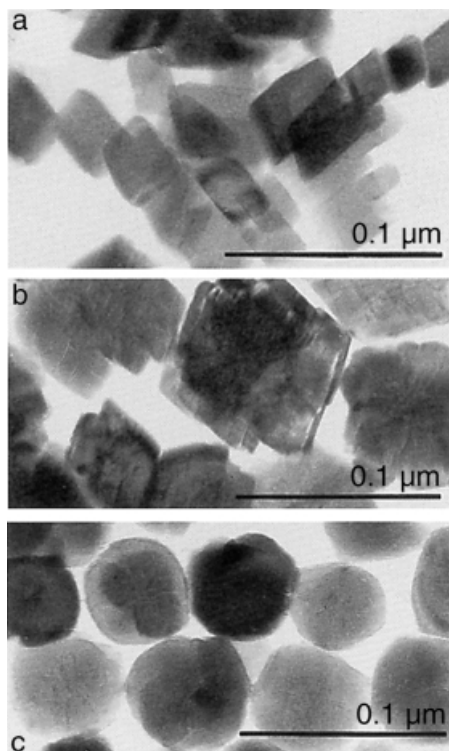


Fig. 4.21 Hematites grown by forced hydrolysis of acid Fe^{III} salt solutions at $98\text{ }^{\circ}\text{C}$ a) from $0.02\text{ M Fe}(\text{NO}_3)_3$; b) from $0.2\text{ M Fe}(\text{ClO}_3)_3$; c) from 0.02 M FeCl_3 . (Schwertmann & Cornell, 2000, with permission).

the surface roughness effect; addition of alcohol to an aqueous solution alters the roughness factor of the different faces and hence their growth mechanisms.

Numerous other additives have also been investigated with respect to their effect on the crystal shape of hematites formed by forced hydrolysis. Of these, surfactants had essentially no effect on particle shape (Kandori et al. 1996), cubes and diamond-like crystals formed in the presence of amines (Kandori et al. 1996) and dioxane (Kandori et al. 1998) and dimethylformamide also led to diamond-shaped crystals (Kandori et al. 1998a). Cu^{II} , Ni^{II} , Co^{II} and Cr^{III} ($\text{Me}/(\text{Me} + \text{Fe}) \leq 0.8$) caused the morphology to change from large spheres to smaller diamonds. It was suggested that the cationic additives prevented the small primary particles from agglomerating to form spheres (Kandori et al. 1998a).

A special method of producing hematites of extremely uniform particle size and shape, in the microsize range, so-called “monodispersed” hematites, has been developed by Sugimoto and coworkers (Sugimoto, 2001). In brief, a concentrated (e.g. 2 M) precipitate from a FeCl_3 solution at a OH/Fe of 2.7, probably ferrihydrite, is aged at $\sim 100\text{ }^{\circ}\text{C}$ (“gel-sol method”). Under these conditions finely dispersed akaganeite is formed first and from this, hematite crystallizes via a subsequent dissolution-recrystallization process. This guarantees a high uniformity of crystal size and shape and a high yield of product. By varying the type and concentration of additives,

platelets, pseudocubes, ellipsoids, and peanut-shaped crystals can be obtained (Fig. 4.22). Whereas chloride led to pseudocubes bounded by {012} faces, sulphate and phosphate promoted ellipsoids bounded by {110} and {100} faces and different sulphate levels also led to peanut-shaped crystals. Various organics including EDTA, NTA, and some dihydroxy benzenes induced formation of ellipsoids (Sugimoto et al. 1998). The experimental conditions are listed in Table 4.4. Uniform crystals are obtained by strictly separating the nucleation phase, where the acicular akaganéite crystals are formed, from the crystal growth of hematite from akaganéite in solution. HRTEM on thin sections of crystals showed that pseudocubes grown in the presence of high levels of chloride ions and the peanuts and ellipsoids grown in the presence of sulphate ions were polycrystalline. The peanuts and cubes consisted of laminar domains 5–20 nm thick (Fig. 4.22 II a & b) (Shindo et al. 1994). Sugimoto & Muramatsu (1996) consider that polycrystals form because the fusion of polynuclei that develop on the surface of the growing crystal nuclei, is blocked by adsorbed chloride and sulphate ions. A similar mechanism was proposed for the formation of polydomainic goethite under conditions of high ionic strength (Cornell & Giovanoli, 1986). Spindles grown in the presence of 0.12 M sulphate by the gel-sol method are covered with tiny whiskers of goethite (Sugimoto & Wang, 1998).

Large, platy hematite crystals form if ferrihydrite is kept under *hydrothermal* conditions. Figure 4.23 a and b show hexagonal plates and discs of hematite up to 20 μm across and 5 μm thick with predominant (001) faces grown in the presence of triethanolamine (TEA) in strongly alkaline media (Sapieszko & Matijevic, 1980). Such crystals also form in the presence of EDTA and KNO_3 at 180 °C in an autoclave (Ozaki et al., 1990) and from poorly crystalline goethite in plain water at 180 °C in 10 days (Fig. 4.23 c). Large platy crystals up to several mm across with predominant {001} faces and well developed (102) and (113) planes have also been produced in 5 M NaOH at 385–485 °C (Kolb et al., 1973).

Plates of micaceous hematite up to 50 μm across are formed by high temperature oxidation of molten Fe^{III} chloride complexes (Carter & Laundon, 1990). Round, hematite single crystals up to 800 μm across and with well defined facets are formed by chemical vapour transport at elevated temperatures (Moukassi et al., 1984). Elongated crystals of hematite with {001} planes predominating and the same morphology as that of the precursor are formed by dehydroxylation of goethite at temperatures between 250 and 500 °C (Duvigneaud & Derie, 1980). At higher temperatures these crystals sinter to irregular masses. Hematite formed by dehydroxylation of akaganéite and lepidocrocite also maintains the morphology of the precursor at low (<300–400 °C) temperature, whereas hematite formed by dehydration of ferrihydrite forms irregular plates.

4.2.6

Magnetite

Natural and synthetic magnetite occurs most commonly as octahedral crystals bounded by {111} planes and as rhombo-dodecahedra (Fig. 4.24). Twinning occurs on the {111} plane (Tab. 4.1). STM examination of the (100) face of a natural sample

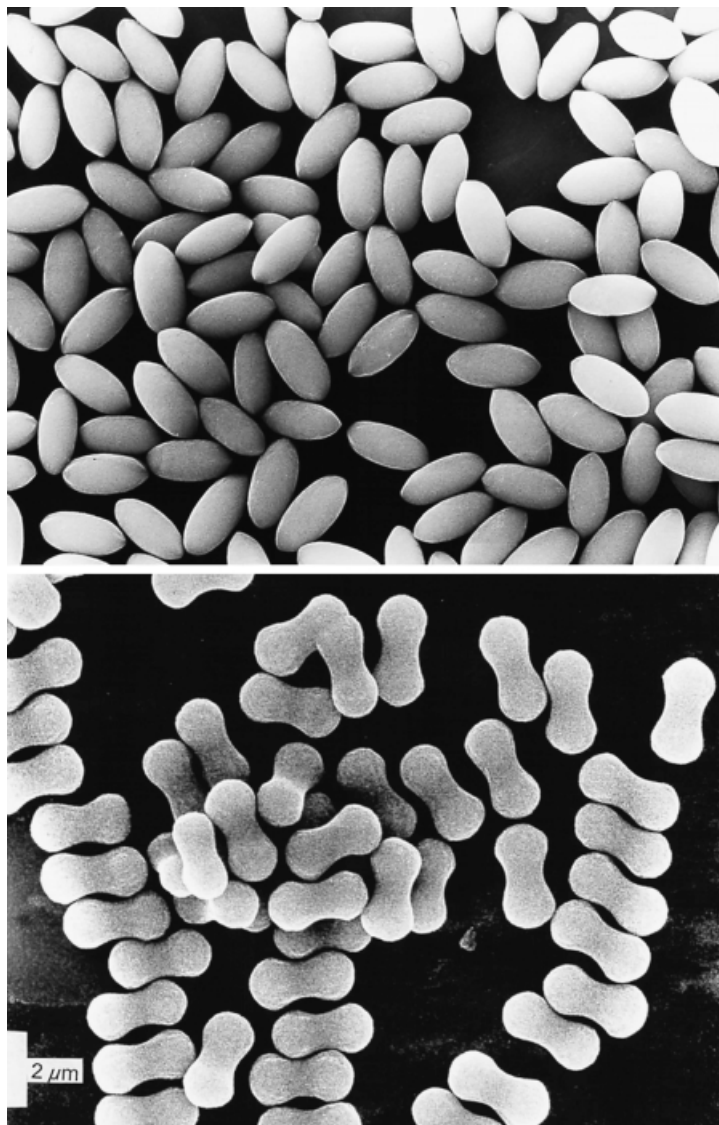


Fig. 4.22 I: Uniform (“monodispersed”) ellipsoidal and peanut-shaped hematites produced by the so-called gel-sol method of T. Sugimoto (Sugimoto et al., 1993, 1998, with permission). II: Polycrystalline internal structure of a pseudo-

cubic (a) and a peanut particle (c) and a HRTEM showing lattice fringes at the polycrystalline margin of a pseudocubic particle (b). (Shindo et al., 1994, with permission) Courtesy T. Sugimoto.

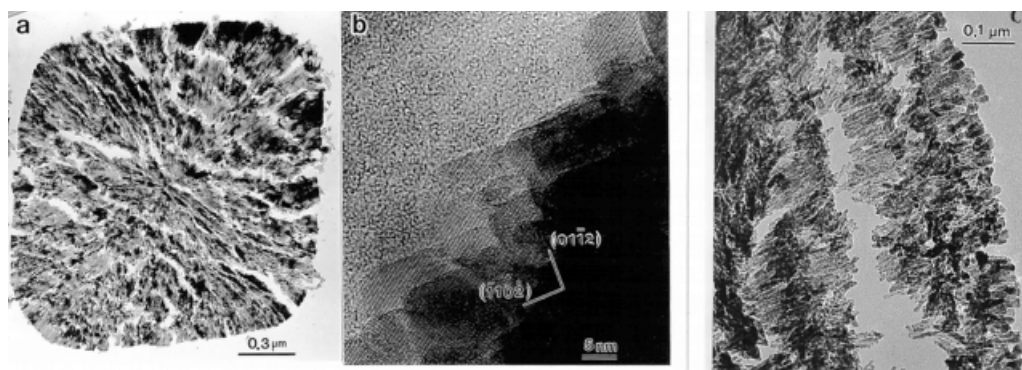


Fig. 4.22 (part II)

Tab. 4.4 Experimental conditions for the production of monodispersed hematites with various crystal shapes (Schwertmann and Cornell, 2000; with permission)

<i>Crystal shape</i>	<i>FeCl₃-solution</i>		<i>NaOH</i>		<i>Aging</i>		<i>Reference</i>
	<i>conc. (M)</i>	<i>amount (ml)</i>	<i>conc (M)</i>	<i>amount (ml)</i>	<i>Temp. (°C)</i>	<i>Duration</i>	
Spheres	0.018	10	0.001 [§]	10	100	24 hr	Matijevic and Scheiner (1978)
Pseudocubes	0.1	100	5.4	100	100	8 days	Sugimoto et al. (1998)
Plates	2.0	40	8	40	180	2 hr	Sugimoto et al. (1996)
Spindles	0.02	1000	0.0003*	1000	100	2 days	Muramatsu et al. (1994)
Peanuts	2.0	100	6.0**	90	100	8 days	Sugimoto et al. (1993)

§ HCl instead of NaOH; * NaH₂PO₄ instead of NaOH; ** plus 10 ml of 0.6 M Na₂SO₄

of magnetite (annealed at 692 °C) showed multiple, cubic terraces with their edges parallel to [110] and with step heights of ca 0.20 nm (Seoighe et al. 1999). On the (111) plane, SEM showed atomically flat terraces up to 100nm in size and separated by monoatomic steps 0.5 nm high. These terraces were oriented along the main crystallographic direction (Shackhutdinov & Weiss, 2000).

Hydrothermal syntheses usually produce single octahedral crystals which can be as large as 10 mm across. In the presence of mineralizers such as 0.1 M HI or 2 M NH₄Cl and at 0.207 MPa at 416–800 °C, magnetite grew as crystals whose shapes were a combination of rhombic dodecahedra ({101} forms) (Heider et al., 1987). The crystals were more rounded than usual. The appearance of the higher forms was considered to result from a decrease in the surface energies caused by the lower surface to volume ratio in the rounded crystals. With formic acid, octahedral crystals 0.1–0.2 mm across have been produced (Viswanathiah et al., 1980). Hydrothermal decomposition of Fe-TEA chelates in the presence of hydrazine (180 °C) produced polydisperse, intergrown octahedra several microns across (Fig. 4.25) (Sapieszko & Matijevic, 1980). The morphology was independent of the type of anion (NO₃⁻, Cl⁻, ClO₄⁻, SO₄²⁻) in the system.

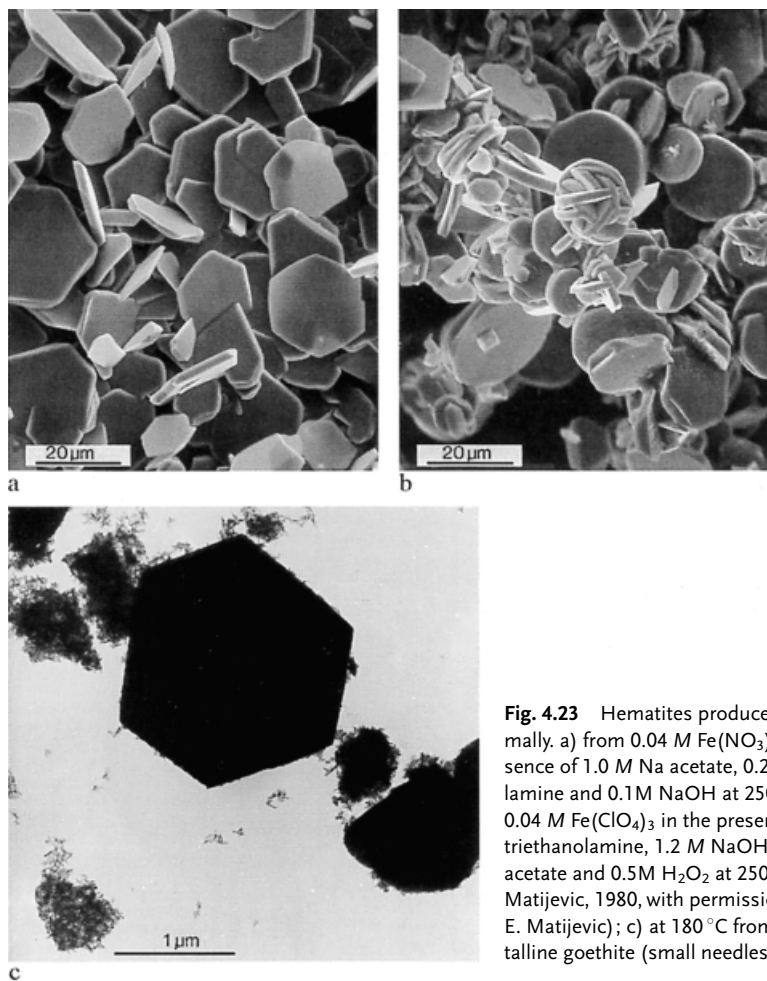


Fig. 4.23 Hematites produced hydrothermally. a) from 0.04 M $\text{Fe}(\text{NO}_3)_3$, in the presence of 1.0 M Na acetate, 0.2M triethanolamine and 0.1M NaOH at 250 °C; b) from 0.04 M $\text{Fe}(\text{ClO}_4)_3$ in the presence of 0.2 M triethanolamine, 1.2 M NaOH, 1.0 M Na acetate and 0.5M H_2O_2 at 250 °C (a & b: Matijevic, 1980, with permission; courtesy E. Matijevic); c) at 180 °C from poorly crystalline goethite (small needles).

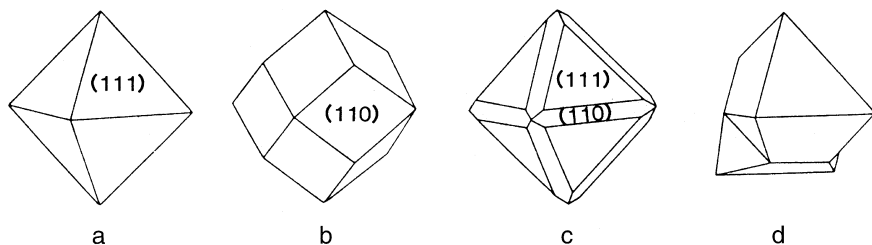


Fig. 4.24 Crystal forms of magnetite. a, c) octahedron; b) rhombododecahedron; d) twin. (Kostov, 1968; with permission).

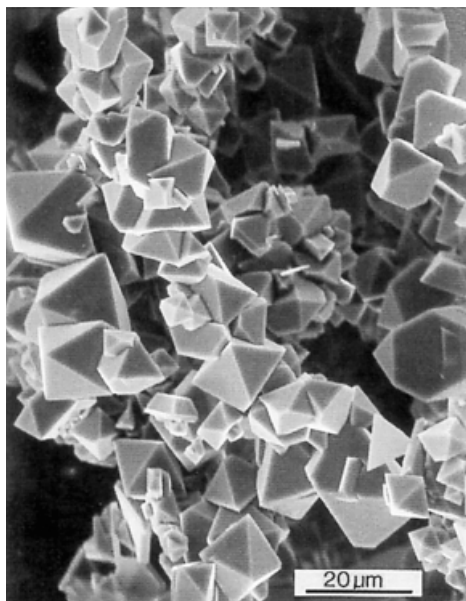


Fig. 4.25 Octahedral magnetite crystals produced hydrothermally at 250 °C from 0.01 M $\text{Fe}_2(\text{SO}_4)_3$ solution in the presence of 0.4 M triethanolamine, 2.4 M NaOH and 0.85 M N_2H_4 (Sapieszko & Matijevic, 1980; with permission; courtesy E. Matijevic).

Syntheses in aqueous systems at temperatures less than 100 °C produce fine-grained (<0.1 μm) rounded, cubic or octahedral crystals (Fig. 4.26). Examples are the oxidation of Fe^{2+} solutions at neutral pH via green rust (Taylor & Schwertmann, 1974; Regazzoni et al., 1981) and the direct precipitation from mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ solutions (pH 4–6) (Sidhu et al., 1978). Larger, fairly uniform octahedra and spheres (0.03–1.1 μm) are obtained if green rust is oxidized with KNO_3 at 90 °C and at pH 6–10 (David & Welch, 1956; Sugimoto & Matijevic, 1980). The initial coagulation of the primary particles was followed by contact recrystallization within the spherical aggregates. The spheres formed when Fe^{2+} was in excess over OH^- , whereas with excess of OH^- (pH 12), cubic crystals formed. Magnetite obtained from $\text{Fe}(\text{OH})_2$ in very basic solution formed largish cubes, that from green rust buffered at pH 8.5 formed thick, little plates and that from $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ solutions raised to pH 13 was deposited as 5 nm particles (Feitknecht, 1959). Magnetite produced by dry reduction of hematite maintains the shape and size of the original hematite particles; both lath-shaped and spherical magnetites have been obtained in this manner.

Metal substituted magnetites (Mn, Co, Cu, Ni) formed from metal substituted ferrihydrites at pH 12 were cubic and 10–50 nm across (Cornell & Giovanoli, 1987a, 1988, 1989; Cornell et al., 1992). Magnetites grown by slow oxidation of green rust at pH 6 in the presence of 0.05–0.10 mol mol⁻¹ phosphate had a well defined octahedral habit with smooth {111} planes; this habit was attributed to stabilization of the planes by adsorbed phosphate; in the absence of the additive, rather irregular crystals formed (Couling & Mann, 1985).

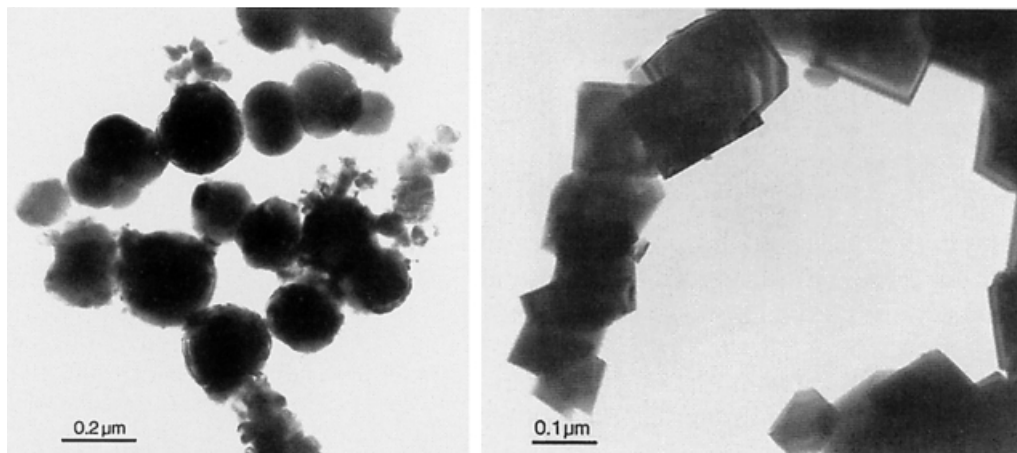


Fig. 4.26 Left: Rounded magnetite crystals obtained by slow oxidation (over 150 days) of a 0.05 M FeCl_2 solution at pH 11.7 and room temperature (Schwertmann & Murad, 1990; with permission); Right: Magnetite octahedra produced by oxidation of a 0.5 M FeSO_4 solution with KNO_3 in 1.43 M KOH at 90 °C (Schwertmann & Cornell, 2000; with permission).

4.2.7

Maghemite

Maghemite is usually formed by solid state transformation from another iron oxide or iron compound and almost always adopts the habit of its precursor. When formed by oxidation of magnetite, either cubic or irregular maghemite particles occur depending on the morphology of the parent material. Maghemite obtained by dehydroxylation of lepidocrocite forms laths elongated in the [101] direction. In fact these laths are polycrystalline aggregates of perfectly orientated crystallites, 7 nm across. Formation of these crystallites is the consequence of the considerable structural strain involved as the lepidocrocite structure is converted to that of maghemite (Giovannoli & Brüttsch, 1975).

Porous, acicular crystals of maghemite with [101] as the long axis form as a result of the transformation series involving dehydroxylation of goethite to hematite, reduction of hematite to magnetite and finally oxidation to maghemite (Berkowitz et al., 1985). In the same way, spindle-shaped, single crystals of maghemite suitable for use in magnetic recording devices have been obtained from spindle shaped hematites (Maeda, 1978; Ozaki & Matijevic, 1985). The particle size of ultrafine maghemites precipitated from $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ solutions can be modified by addition of oleate ions (Davies et al., 1993). Porous, platy crystals with extensive development of the (101) planes have been obtained by transformation of FeOOCH_3 and finely divided plates were produced by decomposition of $\text{N}_2\text{H}_5\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3$ (Morales et al., 1989); the latter case is a rare example of maghemite crystals not maintaining the

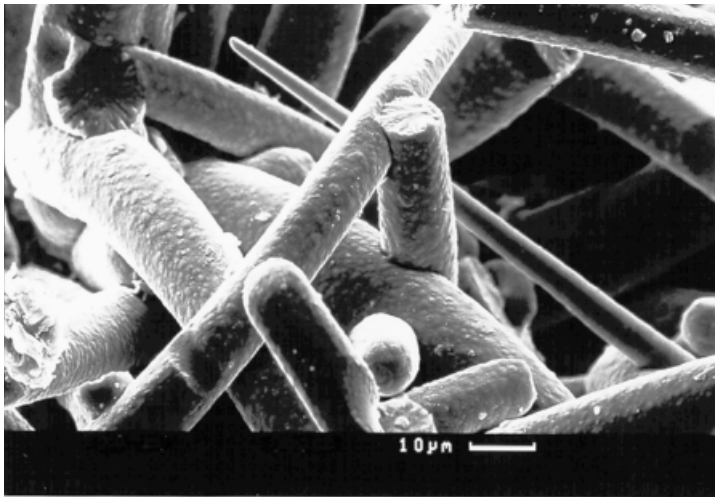
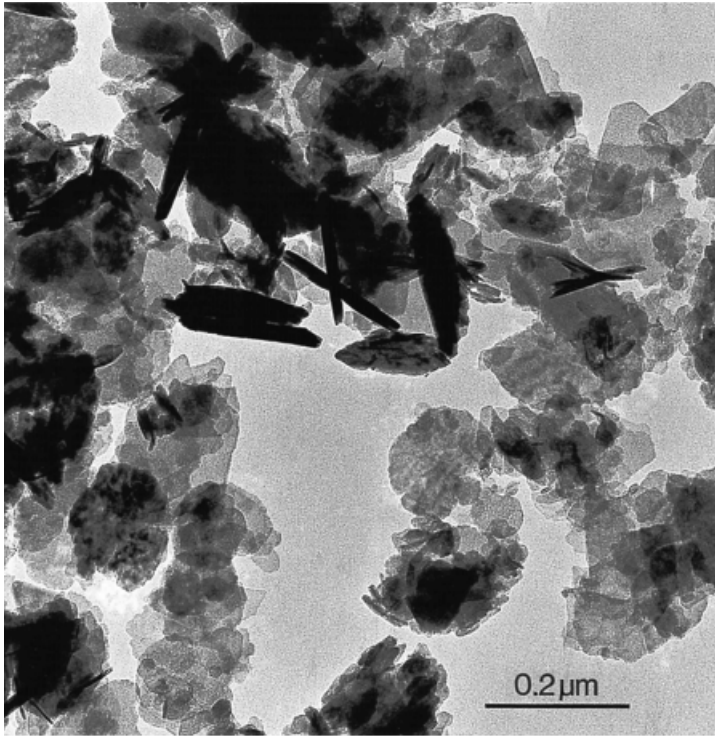


Fig. 4.27 Upper: Platy crystals of synthetic goethite formed by rapid oxidation of FeCl_2 solution at pH 8 (Carlson & Schwertmann, 1980; with permission). Lower: Vermiform natural goethite aggregates from the Clara Mine, Black Forest (Courtesy K. Walenta).

morphology of the precursor. Maghemite precipitates directly as twinned, monodisperse crystals from a vapour phase reaction in an O_2/H_2 flame. The particles produced by this method are bounded by $\{101\}$ and $\{111\}$ faces (Batis-Landoulis & Vergnon, 1983).

4.2.8

Other Iron Oxides

$\delta\text{-FeOOH}$ precipitates as platy crystals. When formed by fast oxidation of $Fe(OH)_2$ at pH 12 well formed hexagonal plates result, whereas simultaneous precipitation/oxidation gives thin plates which are often rolled up (Feitknecht, 1959). Feroxyhyte ($\delta'\text{-FeOOH}$) produced by rapid oxidation (e.g. with H_2O_2) of $FeCl_2$ solution at pH 8 also forms thin platy crystals around 100 nm in size (Fig. 4.27, upper). As the pH is lowered, the crystals become smaller and develop a grassy appearance (Carlson & Schwertmann, 1980). Natural feroxyhyte from the Clara Mine in the Black Forest occurred as vermiform aggregates (Fig. 4.27, lower) (Walenta, 1997).

$Fe(OH)_2$ exists as hexagonal plates as do the *green rusts* (Feitknecht & Keller, 1950; Bernal et al., 1959). The basic morphology of *wüstite* is cubic, but this compound is frequently obtained as very irregular particles. It is formed as irregular rounded crystals 20–100 μm across by reduction of hematite with H_2/H_2O at 800 °C (Moukassi et al., 1984).

5

Surface area and porosity

5.1

Surface Area

The specific surface area of a solid is the surface area of a unit mass of material, usually expressed as $\text{m}^2 \text{g}^{-1}$. There is an inverse relationship between surface area and particle size. Massive crystals of hematite from an ore deposit (e.g. specularite) may have a surface area $\ll 1 \text{ m}^2 \text{g}^{-1}$. As particle size/crystallinity is governed largely by the chemical environment experienced during crystal growth, the surface area of a synthetic iron oxide depends upon the method of synthesis and that of a natural one, upon the environment in which the oxide formed.

The oxide surface has structural and functional groups (sites) which interact with gaseous and soluble species and also with the surfaces of other oxides and bacterial cells. The number of available sites per unit mass of oxide depends upon the nature of the oxide and its specific surface area. The specific surface area influences the reactivity of the oxide particularly its dissolution and dehydroxylation behaviour, interaction with sorbents, phase transformations and also, thermodynamic stability. In addition, specific surface area and also porosity are crucial factors for determining the activity of iron oxide catalysts.

Surface area is a property that can vary according to the method used to measure it. Areas found by gas adsorption may depend upon the size and nature of the probe molecule. A full description of the different methods in use and also their limitations is given in the text of Gregg and Sing (1991).

The BET method (Brunauer, Emmett and Teller, 1938) with N_2 as the adsorbate, is by far the most common method of measuring the surface areas of Fe oxides. Various commercial instruments are available for these measurements. The method involves measuring the extent of adsorption of N_2 (at the boiling temperature of liquid $\text{N}_2 - 77 \text{ K}$) on the outgassed solid as a function of the relative pressure, p/p_0 , i.e. the adsorption isotherm; p is the partial pressure of the adsorbate and p_0 is its equilibrium vapour pressure. The following linear relationship exists between the amount adsorbed, v , ($\text{cm}^3 \text{g}^{-1}$) and the relative vapour pressure, p/p_0 :

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{1}{v(p_0/p - 1)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \cdot \frac{p}{p_0} \quad (5.1)$$

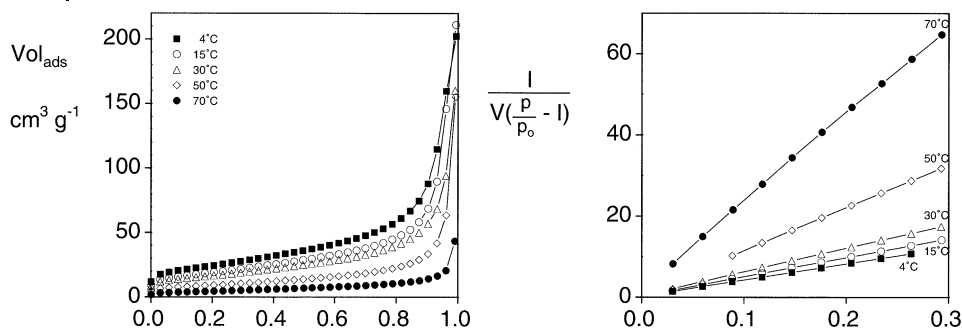


Fig. 5.1 Left: N₂-adsorption isotherms of goethites synthesized at various temperatures; right: BET plots (Weidler, unpubl.).

where v_m is the monolayer capacity of adsorption (B in Fig. 5.3) and c the so called BET constant. c and v_m are obtained from the slope of the plot, s , and the intercept, i , on the ordinate i.e. $v_m = (s + i)^{-1}$ and $c = \frac{s}{i} + 1$. The surface area is then calculated from v_m and the area occupied by one molecule of the adsorbate e.g. $0.162 \text{ nm}^2/\text{molecule}$ for N₂. The BET constant c is related to the energy of adsorption i.e. the difference between the molar heat of adsorption of the first layer and the molar heat of condensation of the adsorbate. As an example, Figure 5.1 (left) shows the original N₂ adsorption curves of five goethites synthesized at 4, 15, 30, 50 and 70 °C and Figure 5.1 (right) shows their BET-plots according to eq. (5.1).

As N₂ is a relatively large molecule, it may not be able to enter small pores. Furthermore, owing to its non ideal gas behaviour, N₂ cannot be used for surface areas $< 1 \text{ m}^2 \text{ g}^{-1}$. These problems can be overcome to some extent by replacing N₂ with water (area $0.108 \text{ nm}^2/\text{molecule}$) which can enter very small pores, or with Ar ($0.138 \text{ nm}^2/\text{molecule}$) which, with a lower saturation vapour pressure, can be used to measure samples with very low surface areas.

The BET method requires that the sample be dried and outgassed to remove adsorbed water. This procedure may, if the outgassing temperature is too high, lead to a phase change at the surface of the oxide hydroxide and hence, an alteration in the specific surface area of the sample. Clausen and Fabricius (2000) recommend that ferrihydrite be outgassed at room temperature, at which temperature, a stable BET surface area is obtained after 19 hr of outgassing.

Other methods of surface area determination depend, in general, on adsorption under well defined conditions of various solute molecules of known dimensions (Sposito, 1984; Davis and Kent, 1990). Some of these are dipole molecules so that dipole interactions with the surface or H-bonding are involved. Water adsorbed at a fixed relative water vapour pressure (e.g. 0.2) to provide a monolayer is one example (Torrent et al., 1990). An organic dipole frequently used for soils is ethylene glycol monoethylether (EGME) (Carter et al., 1965). The main problem with these dipole molecules lies in their mutual association which may lead to localized adsorption beyond a monolayer (capillary condensation), particularly on porous material.

The specific surface area of a crystalline material may also be *calculated* using the average dimensions of the crystals together with the density of the material, i.e.

$$\text{Specific surface area} = \frac{\text{crystal surface area}}{\text{density} \times \text{crystal volume}} \quad (5.2)$$

Methods of measuring crystal size are described in Chapter 4. Agreement between the calculated surface area and the BET surface area to within 10–20% is considered reasonable. For a sample of akaganéite, for example, Naono et al., (1982) calculated a surface area of $26 \text{ m}^2 \text{ g}^{-1}$ from the crystal size and obtained an area of $22.4 \text{ m}^2 \text{ g}^{-1}$ from N_2 adsorption. Calculated areas are, however, lower than measured ones if the crystals are porous. If the size distribution is wide, errors in the calculated area may also arise as a result of omission of the smaller crystals. When the surface area is calculated using the particle size determined by light scattering, it is assumed that the particles are smooth spheres: surface heterogeneity is ignored and the surface area found by this method is therefore, often lower than that obtained by the BET method.

An estimate of the surface area of Fe oxides in a mixture of other fine grained compounds, e.g. in soils or sediments, may be obtained from the crystal size calculated from XRD line broadening using the Scherrer formula (see Chap. 7) or from the difference in area before and after selective removal of the iron oxides divided by the amount of oxides that were extracted (see Chap. 16). The latter method assumes that the areas of the various components are additive (Schwertmann, 1988).

Rarely have the values of surface area obtained by different methods been compared for the same samples. Torrent et al. (1990) measured the surface areas of 31 synthetic goethites of variable crystal size and morphology using N_2 and H_2O adsorption, but averaged the results of the two methods. Ten natural, goethite-rich samples had higher values (on average by 43%) with EGME than with N_2 (Torrent et al., 1992). For 14 natural hematites, the N_2 -surface area ($10\text{--}36 \text{ m}^2 \text{ g}^{-1}$) was lowest followed by the H_2O surface area ($20\text{--}47 \text{ m}^2 \text{ g}^{-1}$) and finally that calculated from the mean crystal size ($21\text{--}90 \text{ m}^2 \text{ g}^{-1}$) (Torrent et al., 1994). A comparison of four methods, viz. N_2 , H_2O , EGME and calculated, is shown for 30 synthetic hematites in Figure 5.2 (Colombo et al., 1994). The last three methods gave values that were significantly correlated with the standard BET- N_2 method, with the H_2O -surface area coming closest to the N_2 -surface area; the EGME values were much higher and the calculated values significantly lower. A very similar relationship was obtained for the surface area SA of 10 synthetic goethites for the N_2 /EGME pair ($\text{N}_2 \text{ SA} = 5\text{--}88 \text{ m}^2 \text{ g}^{-1}$; $\text{N}_2 \text{ SA} = -20 + 1.87 \cdot \text{SA}_{\text{EGME}}$ with $r^2 = 0.986$) (P. Weidler, pers. comm.). The EGME dipole appears to form more than a monomolecular layer, particularly on rough surfaces, whereas the calculated area is based on a smooth surface and may, therefore, be underestimated.

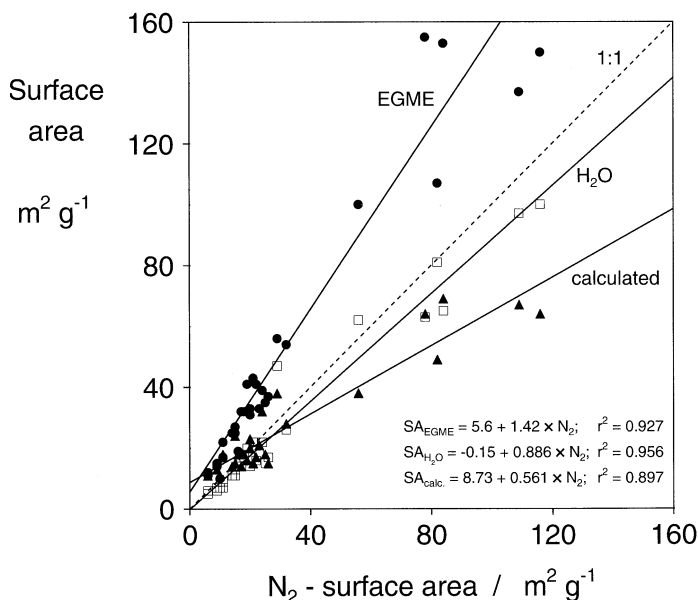


Fig. 5.2 Comparison of four different methods for surface area determination using 30 synthetic hematites (Colombo et al., 1994).

5.2

Porosity

Porosity refers to the volume of pores in a solid. It contributes to the “internal” surface area of the sample and can influence the kinetics of adsorption. Diffusion into and out of pores is often considered responsible for slow adsorption and desorption processes. Pores vary in size and shape. They have been classified according to their average widths as *micropores* which are of the order of molecular dimensions ($< 2 \text{ nm}$), *meso- or transitional pores* which are between $2\text{--}50 \text{ nm}$ and *macropores* which are larger than 50 nm (Sing et al., 1985). The sum of all the pores is called the pore volume (porosity).

Pores may be present as structural features (e.g. between domains) or as a result of aggregation of particles. They may also be the result of partial dehydroxylation (oxide hydroxides) or dissolution. Although the shapes of pores can be quite variable, there are some definite, basic forms. The commonest of these are; 1) slit shaped, the walls of which may or may not be parallel; 2) ink bottle which are closed upon all sides but one from which a narrow neck opens and 3) cylindrical. Upon partial dissolution, pores bounded by well-defined crystal planes (e.g. $\{102\}$ in goethite) develop (Chap. 12).

Each type of pore is associated with a characteristic type of adsorption isotherm. The appropriate method of characterizing the porosity of an iron oxide is, therefore, to obtain the complete adsorption/desorption isotherm. There are six standard adsorption isotherms for gases (Fig. 5.3). Type I, with enhanced adsorption at low relative

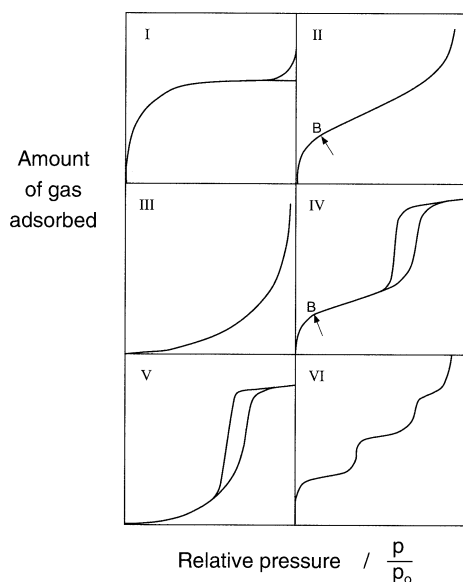


Fig. 5.3 Six types of adsorption isotherms. Type IV and V possess a hysteresis loop, the lower branch of which represents adsorption and the upper branch desorption of the gas (from Gregg & Sing, 1991; with permission). B marks the point where a monolayer adsorption is complete.

pressures, indicates a high adsorption energy at low saturation and microporosity; the limiting amount of uptake corresponds to the micropore volume. A type II isotherm as in Figure 5.1 is associated with a nonporous or mesoporous sample and corresponds to multilayer adsorption. The inflection point, B, indicates the point of completion of the monolayer. A type III isotherm indicates weak adsorbate/adsorbent interactions. The type IV isotherm is characterized by a hysteresis loop caused by capillary condensation: this is used for determination of pore size. A type V isotherm is similar to type IV, but indicates weaker interactions and a type VI isotherm is associated with stepwise, multilayer adsorption of for example, He, on a uniform substrate.

The shape of the hysteresis loop in the adsorption/desorption isotherms provides information about the nature of the pores. The loops have been classified according to shape as A, B and E (De Boer, 1958) or as H1 – H4 by IUPAC (Sing et al., 1985). Ideally, the different loop shapes correspond to cylindrical, slit shaped and ink-bottle pores; the loops in the isotherm IV and V of Figure 5.3 correspond to cylindrical pores. Wide loops indicate a broad pore size distribution (for an example see Fig. 14.9). The absence of such a loop may mean that the sample is either nonporous or microporous. These generalizations provide some initial assistance in assessing the porosity of a sample. In fact the adsorption/desorption isotherms are often more complicated than those shown in Figure 5.3 owing to a mixture of pore types and/or to a wide pore size distribution.

A reliable way of identifying the existence of micro- and mesoporosity and of estimating pore volume is the t-plot analysis of de Boer et al. (1966). The amount of gas adsorbed by the test material is related to the amount adsorbed by a non porous reference material. For the latter, there is a linear relationship between the amount adsorbed, v , and the average thickness of the adsorbed layer, t , i. e.

$$t = t_m \cdot \frac{v}{v_m} \quad (5.3)$$

where t_m is the average thickness of a monolayer (0.345 nm for N_2) and v_m is the multilayer adsorption capacity (t is in nm, v and v_m in $\text{cm}^3 \text{g}^{-1}$ at STP). This is the case for the goethites shown in Fig. 5.1; their t -plots are fully linear and extrapolate to zero – the samples are essentially nonporous. In cases where porosity only develops upon dehydration, such as in the $\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3$ conversion, the starting sample may serve as the reference material. The t -plot of a porous sample has two linear sections; the slope of the initial, steeper part reflects the total sample surface area, whereas the external surface area can be taken from the (lower) slope of the second part of the plot. The surface area due to porosity, S_p , is the difference between the two slopes. The micropore volume, V_p , is taken from the intercept of the second section of the plot on the ordinate. The average pore diameter, d , may then be calculated from $d = 2V_p/S_p$.

An example involving the akaganéite $\rightarrow$ hematite transformation is shown in Figure 14.8 where the average pore diameter increased from 1.1 nm at 150 °C to 3.7 nm at 350 °C and then to > 15 nm at 500 °C. The t -plot method using H_2O as an adsorbate has also been used to investigate the location of H_2O in the tunnel structure of akaganéite (Naono et al., 1993).

A similar graphical method is the so-called α plot of Sing (1976; and see Gregg and Sing, 1991). This plots the amount of N_2 taken up by the test solid as a function of α which is obtained from the reference isotherm:

$$\alpha = \frac{N_2 \text{ adsorbed at any } p/p_0}{N_2 \text{ adsorbed at } p/p_0 = 0.4} \quad (5.4)$$

It is assumed that capillary condensation sets in at p/p_0 of 0.4. Whereas the curve for a nonporous reference sample passes through the origin, the one for a porous material is shifted upwards. This method avoids the need to determine the layer thickness and the area occupied per molecule.

5.3

Surface Roughness and Fractal Dimensions

The surface of a crystal often shows irregularities such as steps, kinks and holes. As microscopic resolution increases, smaller and smaller irregularities become visible. If similar surface morphologies are observed on all scales, regardless of magnification, these surfaces are termed self-similar or self-affine.

When measuring the area of such surfaces using the BET method and probe molecules of different cross sectional area, σ_0 , the specific surface area, SA , as a function of σ_0 will obey a power law (Avnir et al., 1983)

$$SA \propto \sigma_0^{(2-D_s)/2} \quad (5.5)$$

in which D_s is called the fractal dimension. D_s varies from 2 for atomically flat surfaces to 3 for sponge-like materials. In other words, the surface area increases as the cross section of the sorbate decreases (for examples, see Farin and Avnir, 1989). In recent years quite a few methods of determining D_s from adsorption measurements have been put forward. These are summarized in Pfeifer and Avnir (1983) and Avnir (1989). An in depth treatment of fractals in nature is given in Mandelbrot (1982).

According to eq. (5.5), a linear relationship, the slope of which is characterized by D_s , is expected between σ_0 and $\log A$. To establish such a relationship, the size of the probe molecule should vary by at least one order of magnitude. If, however, the variation is restricted to less than an order of magnitude, surface roughness instead of self-similarity might be a more appropriate term.

To overcome the problems which arise from a limited size range and the different adsorption properties of different adsorbates, one may use the entire adsorption isotherm obtained with just one probe molecule instead. There are two approaches both leading to a Frenkel-Halsey-Hill type equation:

$$\Theta = K \cdot [\ln (p_0/p)]^{-\nu} \quad (5.6)$$

where Θ is the relative adsorption, K is a constant and the exponent ν is related to D_s . Pfeifer et al. (1989) found $\nu = (3 - D_s)/3$ and Avnir and Jaroniec (1989) $\nu = 3 - D_s$. Both models are based on the basic property of a fractal surface, viz. that the number of molecules, N , necessary to form a monolayer depends upon the size, d , according to $N = d^{D_s}$. In these equations, therefore, the yardstick used is the thickness of the adsorbed layer as a function of the partial pressure, p/p_0 . The difference between the two models may be due to surface tension effects which are not fully considered in the appropriate theories; this is still a matter of debate (Ismail and Pfeifer, 1994).

Other possible methods of obtaining fractal dimensions are light- and small-angle-X-ray-scattering (SAXS). The first method gives information about mass fractality of aggregates and aggregation kinetics (Fleischmann et al., 1990), whereas the latter allows mass and surface fractals to be differentiated (Schmidt, 1990).

Fractal dimensions of synthetic goethite obtained by small angle X-ray scattering (SAXS) were in agreement with the values calculated using the equation of Avnir and Jaroniec (Weidler et al., 1995 a). Values of D_s , mentioned in later section have been obtained using this equation.

5.4

The iron oxides

The particle size and thus surface area of iron oxides and also the porosity depend strongly on the conditions under which crystal growth takes place. For example, high rates of growth at low temperatures may lead to poorly ordered crystals with surface areas of up to several hundred $\text{m}^2 \text{g}^{-1}$, whereas low surface area crystals may grow at higher temperatures and at slow rates of formation. In natural environments, such ex-

tremes may exist in soils on the one hand and under hydrothermal conditions on the other. Synthetic methods allow crystal growth and thereby surface area, to be manipulated to some extent. Numerous experiments have identified such factors as temperature, source of Fe (Fe^{II} , Fe^{III} or Fe complexes), the presence of interfering or substituting ions such as Al, Mn and Si and organics and even stirring as against no agitation, as having a marked influence on growth. As particle size is the result of interactions between these various factors, it can be difficult to predict the surface area of a particular preparation, although some generalisations are possible.

5.4.1

Goethite

The surface areas of both natural and synthetic goethites range from ca. 8 to 200 $\text{m}^2 \text{g}^{-1}$. XRD line broadening techniques indicate that soil goethites have surface areas of from 20 to 200 $\text{m}^2 \text{g}^{-1}$ (Schwertmann, 1988). On the other hand, massive (museum) specimens may consist of mm sized crystals with surface areas well below 1 $\text{m}^2 \text{g}^{-1}$.

The surface area (EGME) of goethite grown from ferrihydrite in 0.7 M KOH decreased from 153 $\text{m}^2 \text{g}^{-1}$ at 4 °C to 9 $\text{m}^2 \text{g}^{-1}$ at 60–90 °C (Schwertmann et al., 1985); the BET method gave different values (88–15 $\text{m}^2 \text{g}^{-1}$), although the same trend with temperature was noted (Weidler, pers. comm.). The surface areas of the high area samples could be lowered by hydrothermal treatment at 150–180 °C due to recrystallisation (termed “healing”) (Schwertmann et al., 1985; Strauss et al., 1997). The recrystallisation process eliminated domains and serrated edges, while the overall crystal size remained essentially the same; it also lowered the micropore volume from 0.6 to 0.06 volume % and the mean micropore diameter from 1.4 to 0.4 nm (Weidler, 1996). Twinned goethite crystals are often several μm in size and have comparatively low surface areas of $\leq 40 \text{ m}^2 \text{g}^{-1}$. The surface areas of samples of acicular crystals grown from ferrihydrite at pH 12 and 70 °C ranged from 30–90 $\text{m}^2 \text{g}^{-1}$ (Atkinson et al., 1968; Cornell et al., 1974). Goethites produced by hydrolysis of acidic Fe^{III} solutions (see Fig. 4.7) had surface areas of ca. 100 $\text{m}^2 \text{g}^{-1}$ (Morup et al., 1983; Glasauer, unpubl.). The BET water vapour area of such a goethite was lower (45 $\text{m}^2 \text{g}^{-1}$) than the N_2 (71 $\text{m}^2 \text{g}^{-1}$) probably because water uptake by the outgassed sample (up to the monolayer B point) corresponds at least in part, to rehydroxylation of the surface and this consumes less water (Koch and Moller, 1987).

High surface areas (80–150 $\text{m}^2 \text{g}^{-1}$) are also reported for goethites formed by *oxidation of Fe^{II} systems* at pH 6–7 and room temperature, whereas those grown at pH 12 have lower areas of around 30 $\text{m}^2 \text{g}^{-1}$ (Torrent et al., 1990).

The effect of *aluminium* on the surface area of goethite depends on the level of Al in the system and on the source of iron. Other conditions being equal, Al reduces both the rate of growth and the crystal size: its effect on surface area depends on which of these two effects predominates. The surface area (EGME) of goethite grown from ferrihydrite in 0.3 M KOH at 25 °C dropped from 52 to 26 $\text{m}^2 \text{g}^{-1}$ as the extent of Al substitution rose from 0 to 0.16 mol mol⁻¹ (Schulze and Schwertmann, 1987). This effect was attributed to an increase in crystal thickness along the [001] direction

together with a reduction in the number of domains per crystal as the substitution rose. When the level of substitution exceeded $0.16 \text{ mol mol}^{-1}$, the specific surface area rose because, although the crystals, were now single domain (cf. Chap. 4), the sizes were greatly reduced. Al markedly impaired growth of goethite formed from Fe^{III} systems in slightly acid to neutral media and areas of $200\text{--}300 \text{ m}^2 \text{ g}^{-1}$ were obtained. High alkalinity (pH 12) overcame this interference and somatoids with an area of $30\text{--}50 \text{ m}^2 \text{ g}^{-1}$ resulted (Schwertmann and Cornell, 2000). Adsorption of *phosphate* reduced the BET (N_2) surface area of goethite from 33 to $25 \text{ m}^2 \text{ g}^{-1}$ (Anderson et al., 1985). This effect was attributed to bridging of the goethite needles by adsorbed phosphate to form aggregates that could not be penetrated by N_2 .

N_2 adsorption isotherms for samples with acicular crystals were type II and gave no indication of there being meso- or microporosity (Naono & Fujiwara, 1980; Naono et al., 1987). Torrent et al., (1990) also found no evidence of porosity for 15 synthetic goethites grown from both Fe^{II} and Fe^{III} solutions (pH 6–12). Some meso- and macroporosity, presumably arising from interparticular pores has, however, occasionally been reported (Davis and Kent, 1990; Boily et al., 2001). The latter authors reported a median micropore diameter of ca. 0.8 nm and macropores 2–4 nm across. AFM examination showed that a multidomainic goethite (BET area $75 \text{ m}^2 \text{ g}^{-1}$) had wedge-like pores longer than 100 nm at the domain boundaries (Fischer et al., 1996). These pores were 4–6 nm deep and 20–30 nm wide. The N_2 adsorption or desorption isotherms showed hysteresis at high relative pressures and appeared to be type IV. The N_2 isotherms of raft-like goethite grown in acidic media were intermediate between type II and type IV with hysteresis at high relative pressures indicating the presence of open-ended, cylindrical macropores which are considered to exist between the crystallites in the rafts (Koch and Moller, 1987).

During dehydroxylation, the surface area of goethite usually rises initially as the expulsion of water leads to the progressive formation of slit-shaped micropores and falls rapidly upon heating above $300\text{--}350^\circ\text{C}$ as the micropores are transformed into mesopores and sintering takes place (see Chap. 14). Naono et al., (1987) reported that a maximum in surface area ($151 \text{ m}^2 \text{ g}^{-1}$) was reached after heating a natural goethite sample for 2 hr at 300°C *in vacuo*. Similar observations have been recorded for synthetic samples heated in air. The transformation to hematite at this stage is almost complete. Naono et al., (1987) also reported that the average width of the micropores as determined by electron microscopy was twice that found by t-plot analysis of the N_2 adsorption/desorption isotherms because the electron beam causes broadening of the pores. Fractal dimensions (D_s) were around 2.55 for goethites synthesised in 0.3 M KOH at between 4 and 50°C and 2.44 for synthesis temperatures of 80°C . Hydrothermal treatment at 180°C lowered the D_s from 2.56 to 2.44 which corresponded to a loss in surface roughness (Weidler et al., 1995).

5.4.2

Lepidocrocite

Surface areas of synthetic lepidocrocite range from 15 to $260 \text{ m}^2 \text{ g}^{-1}$ depending on the conditions of synthesis (Schwertmann, 1973). Low area samples are obtained by

oxidation of Fe^{II} systems at pH 6–7 with the area increasing as the pH falls to 5 (Schwertmann and Taylor, 1972a; Giovanoli and Brüttsch, 1975; Schwertmann and Thalmann, 1976). Samples synthesised in the presence of organics (pyridine or urotropin) and also silicate, have surface areas which exceed $100 \text{ m}^2 \text{ g}^{-1}$ (Schwertmann and Thalmann, 1976; Brauer, 1982; Gomez-Villacieros, 1987). Lepidocrocite illustrates the effect of crystal shape as well as size (see Chap. 4) on surface area. Lath-shaped crystals elongated along [100] and with smooth, terminal (101) faces have surface areas of $20\text{--}30 \text{ m}^2 \text{ g}^{-1}$, whereas crystals of similar size gain additional surface area from the highly serrated terminals (Schwertmann and Thalmann, 1976). The serrated edges could be removed by recrystallization to cubic crystals in KOH in the presence of silicate species, upon which the surface area dropped from 58 to $17 \text{ m}^2 \text{ g}^{-1}$ (Schwertmann and Taylor, 1972a).

A well crystallized lepidocrocite with smooth edges (surface area $32.5 \text{ m}^2 \text{ g}^{-1}$) was nonporous and displayed a reversible type II N_2 adsorption isotherm (Gomez-Villacieros et al., 1984). Poorly crystallized, high surface area material also has a type II adsorption isotherm, but with B type hysteresis; this material contained mesopores $2\text{--}20 \text{ nm}$ across (Crosby et al., 1983; Madrid and De Arambarri, 1985). Lepidocrocite crystals with highly serrated terminals had a surface area of $67 \text{ m}^2 \text{ g}^{-1}$ of which 13% could be attributed to micropores ca. 1.5 nm across (Weidler, 1995).

Upon thermal dehydroxylation, *in vacuo* and in air, lepidocrocite behaves similarly to the other iron oxide hydroxides. With rising temperature, the surface area rises as slit-shaped micropores develop and decreases at higher temperatures (350°C) as micropores change to mesopores (Giovanoli and Brüttsch, 1975; Gomez-Villacieros et al., 1984; Naono and Nakai, 1989). In the case of a well crystallized material the surface area rose from $32 \text{ m}^2 \text{ g}^{-1}$ initially to $68 \text{ m}^2 \text{ g}^{-1}$ at 300°C by which temperature complete conversion to microporous maghemite had occurred; the mesoporous hematite produced at 415°C had a surface area of $64 \text{ m}^2 \text{ g}^{-1}$ (Gomez-Villacieros et al., 1984). The width of the micropores derived from both N_2 isotherms and TEM ranged from 0.17 to 7 nm ; the higher values were obtained by TEM.

5.4.3

Akaganéite and schwertmannite

The surface area of akaganéite also depends upon the crystal shape (see Chap. 4). Samples of somatoidal crystals usually have an area of between $20\text{--}60 \text{ m}^2 \text{ g}^{-1}$, whereas areas of rod-like crystals range from $100\text{--}150 \text{ m}^2 \text{ g}^{-1}$. Type II (Paterson and Tait, 1977; Naono et al., 1982) and type IV N_2 isotherms (Gonzalez-Calbet et al., 1981) have been reported for the somatoids. Isotherms for the rod-like crystals were type IV and non reversible (Paterson and Tait, 1977).

The crystals of akaganéite are not microporous. Micropores observed by TEM are considered to be due to irradiation in the electron beam (Galbraith et al., 1979; Naono et al., 1982). Open ended, cylindrical, interparticular micropores have been reported; these arose as a result of alignment of the rod-like crystals into parallel arrays (Paterson and Tait, 1977). Akaganéite does possess a potential structural microporosity arising from the presence of $0.21\text{--}0.24 \text{ nm}$ across tunnels in the structure. At room

temperature, these tunnels are filled with water and chloride ions, but after evacuation at 150 °C, N₂ adsorption at low relative pressures increased markedly (Gonzalez-Calbet et al., 1981). This behaviour was attributed to evacuation of water from the tunnels and its replacement by N₂. Different behaviour was reported by Naono et al., (1993). From the much higher adsorption of H₂O than N₂, they concluded that the N₂ molecule (0.43 nm in size) cannot enter the tunnels, whereas the H₂O molecule (0.23 nm) can. The volume of H₂O adsorbed in the tunnels, which was obtained from a t-plot, was 16.3 mm³ g⁻¹. This value is in excellent agreement with the calculated tunnel space of 17 mm³ g⁻¹. These results suggest that chloride cannot be in the tunnels and must be located somewhere else in the structure, probably in the ligand shell of the Fe^{III} atom.

The effect of thermal dehydroxylation on surface area and porosity appears to depend to some extent on the atmosphere under which it is carried out, on the time and temperature and upon the characteristics (water and chloride levels) of the sample. In general, however, slit shaped micropores develop initially upon heating and the surface area rises (Gonzalez-Calbet et al., 1981; Naono et al., 1982). As the temperature increases, the micropores coalesce to mesopores, the temperature at which these changes take place depends on the conditions mentioned above, but is lower than 500 °C. Naono et al. (1982) found that upon dehydroxylation in vacuo the sample surface area increased from 55 to 177 m² g⁻¹ as the temperature increased to 250 °C; slit-shaped micropores 0.8 nm across developed leading to a highly porous, seemingly amorphous phase. At higher temperatures (550 °C) hematite formed and the surface area dropped to 22 m² g⁻¹ accompanied by conversion of the micropores to meso- and macropores.

Data concerning the surface area of *schwertmannite* is limited. Due to the poor crystallinity, the areas are very high and range from 240–320 m² g⁻¹ (EGME) for synthetic samples and from 125–225 m² g⁻¹ for natural ones (Bigham et al., 1990).

5.4.4

δ-FeOOH and feroxyhyte

Synthetic δ-FeOOH has a surface area which ranges from 20–300 m² g⁻¹ depending on the thickness of the crystals. In a series of seven synthetic feroxyhytes the surface area increased from 140 to 240 m² g⁻¹ (EGME method) as the crystallinity decreased (Carlson and Schwertmann, 1980). δ-FeOOH displays interparticle porosity, i.e. slit-shaped micro- or mesopores between the plate like crystals (Jimenez-Mateos et al., 1988; Ishikawa et al., 1992). Both TEM observations and t-plot analysis showed that 0.8 nm micropores formed upon dehydroxylation at 150 °C in vacuo. The surface area rose steeply as the temperature exceeded 100 °C and reached a value close to 150 m² g⁻¹ at 200 °C at which temperature, the sample was completely converted to hematite.

5.4.5

Ferrihydrite

Surface areas of ferrihydrite have been determined by a wide range of methods and are reported as varying between 100 and 700 m² g⁻¹ (Table 5.1 see also Jambor & Dutrizac, 1998). The BET method is widely used; for natural samples this gives areas of between 200–400 m² g⁻¹.

The small, spherical particles of ferrihydrite often pack together to form aggregates > 0.1 µm across. The aggregated structure and interparticle porosity create difficulties in measurement of surface area because the internal area is not fully accessible to all measurement techniques. It is rare for more than two methods of area measurement to have been applied to the same sample. Pyman and Posner (1978) obtained an area of 250 m² g⁻¹ using both N₂ and water BET measurements. With the EGME method, however, the same sample had an area of 600 m² g⁻¹. These

Tab. 5.1. Surface areas of ferrihydrites by different methods.

<i>Method</i>	<i>Surface area (m²g⁻¹)</i>	<i>Comment^{a)}</i>	<i>Reference</i>
BET Ar	215–270		Van der Giessen, 1966
H ₂ O	300 (± 50)		Davies-Colley et al., 1984
P ads.	720		Anderson and Malotky, 1979
Neg. ads. Na ⁺ pH 4	270–335		Davis and Leckie, 1978
Neg. ads. Mg ²⁺ pH 5	700		Avotins, 1975
BET-N ₂	340	} synthetic 2-line	Eggleton and Fitzpatrick, 1988 Weidler, 1995
	176; 313		
EGME	390		
BET-N ₂	269		Bruun Hansen et al., 1994
BET-N ₂	230		Axe and Anderson, 1995
BET-N ₂	225	} synthetic 6-line	Eggleton and Fitzpatrick, 1988 Stanjek and Weidler, 1992 Weidler, 1995
	203		
	204		
EGME	390		Eggleton and Fitzpatrick, 1988
BET-N ₂	205		Larsen and Postma 2001
TEM	250		Tipping, 1981
Fitting parameter for Triple-layer model	600–700		Davis and Leckie, 1978
BET-Ar	68–425	natural	Carlson and Schwertmann, 1981
EGME	221–560	2–6-line with 1.3–5.5% C org.	Carlson and Schwertmann, 1981

a) If not specified, the sample is probably 2-line ferrihydrite (so called hydrous ferric oxide, HFO)

authors considered that with the latter method the point of monolayer coverage was not distinct enough to determine when a monolayer had formed, thus leading to anomalously high results. Other authors consider that the EGME surface area is higher than that obtained using the BET method either because the interior of the aggregates is more accessible to the ether dipole than to the N_2 molecule or because, particularly in fine pores, the dipole forms more than a monolayer coverage.

Another problem is the physical pretreatment of the sample with respect to grinding and the temperature and duration of the outgassing procedure. A decrease in surface area of a 2-line ferrihydrite was found after grinding the freeze-dried material in acetone and an area increase with increasing outgassing temperature (25 vs. 50 °C) (Weidler, 1995). It was suggested that acetone is difficult to remove during outgassing.

Other methods used to determine the area of ferrihydrite include negative adsorption of Mg^{2+} and Na^+ and phosphate adsorption, which, like the above methods gave areas ranging from 300–700 $m^2 g^{-1}$. These higher values are in line with the observation that phosphate can penetrate into the ferrihydrite aggregate (Willett et al., 1988). Davis and Leckie (1978) estimated surface area by using it as an adjustable parameter in the triple layer model for adsorption (see Chap. 11) and obtained a value of ca. 650 $m^2 g^{-1}$. A value of ca. 600 $m^2 g^{-1}$ was also obtained from extrapolation of a linear correlation between the initial rates of microbial dissolution and the surface areas of a range of Fe oxides (Pichler & Veitzer, 1999).

A negative correlation has been found between carbon content and surface area (EGME) for natural ferrihydrites. The organic matter probably promotes aggregation of the particles. Upon removal of organics by H_2O_2 treatment, the surface area of the organic free material increased by as much as 170 $m^2 g^{-1}$ (Schwertmann and Fischer, 1973; Süsser and Schwertmann, 1983). Synthetic ferrihydrite produced by oxidation of an Fe^{III} citrate complex also had a surface area lower than 100 $m^2 g^{-1}$ and this was attributed to citrate binding.

Due to aggregation of particles, ferrihydrite is microporous, i.e. the porosity is interparticular. Ferrihydrite precipitated at pH 8 from Fe^{III} solution displayed a type IV isotherm with type E hysteresis (Crosby et al., 1983). The freshly precipitated material contained ink bottle pores 2–5 nm in diameter. Larger pores (ca. 20 nm) developed over an 11 day period. Between 83 and 95 % of the total pore volume of a 2-line ferrihydrite was found to be due to micropores (Weidler, 1995).

Heating microporous ferrihydrite in air at 100 °C transformed it to a mesoporous substance with cylindrical pores (Cornejo, 1987) as indicated from the hysteresis loops in the N_2 isotherms (see Chap. 14). The change in porosity was due to expulsion of water. At temperatures higher than 150 °C transformation to hematite occurred and slit-shaped mesopores developed. During the transformation process the surface area of a 2-line ferrihydrite fell from 235 to 218 $m^2 g^{-1}$ at 100 °C; the mesoporous hematite obtained at 150 °C had an area of 178 $m^2 g^{-1}$ and the well crystallized material produced at 350 °C had an area of 46.7 $m^2 g^{-1}$. For a 6-line ferrihydrite a reduction in area from 203 to 125 $m^2 g^{-1}$ was observed after 96 h heating at 123 °C (Stanjek and Weidler, 1992). When following a phase transformation such as this, the BET method certainly seems the most appropriate one for monitoring the change in surface area.

5.4.6

Hematite

The surface area of synthetic hematite depends upon whether the oxide was produced by calcination or grown in solution. The temperature of (dry) heating influences the surface area. Hematites produced at 800–900 °C have areas $< 5 \text{ m}^2 \text{ g}^{-1}$ due to sintering of the particles. Hematites obtained by dehydroxylation of the various polymorphs of FeOOH or ferrihydrite at temperatures lower than 500–600 °C are mesoporous and have much higher surface areas – up to $200 \text{ m}^2 \text{ g}^{-1}$. Commercial hematites are usually produced by calcination and hence have a low surface area.

Hematites grown from solution at temperatures less than or around 100 °C have areas ranging from $10\text{--}90 \text{ m}^2 \text{ g}^{-1}$ depending on particle size and shape. Idiomorphic crystals ca. $1 \mu\text{m}$ in size can be grown in strongly alkaline solutions and their surface areas are as low as $2 \text{ m}^2 \text{ g}^{-1}$ (Torrent and Schwertmann, 1987; Schwertmann and Cornell, 2000). The surface areas of spherical crystals grown by forced hydrolysis of Fe^{III} solutions at 100 °C, as measured by N_2 and water adsorption and also calculated from crystal size, were in reasonable agreement (Tab. 5.2), whereas for the cubic particles, the water surface area was three times as great as the N_2 area due to capillary condensation (Kandori et al., 1991).

Hematite prepared by the sol-gel method had low surface areas. The BET area of a sample of ellipsoidal crystals ($3.3 \mu\text{m}$ length, $1.2 \mu\text{m}$ width) was $12.4 \text{ m}^2 \text{ g}^{-1}$, that of a sample of pseudocubes ($1.4 \mu\text{m}$ edge length) was $2.65 \text{ m}^2 \text{ g}^{-1}$, that of thick platelets ($2.8 \mu\text{m}$ diameter, $0.5 \mu\text{m}$ thickness) was $2.10 \text{ m}^2 \text{ g}^{-1}$ and that of thin platelets ($13.3 \mu\text{m}$ diameter, $1.5 \mu\text{m}$ thickness) was $0.7 \text{ m}^2 \text{ g}^{-1}$: the classification of the platelets appears to refer to their aspect ratios (Sugimoto and Wang, 1998). Hematite rich soil samples had surface areas of $10\text{--}36 \text{ m}^2 \text{ g}^{-1}$ (BET- N_2) and $12\text{--}42 \text{ m}^2 \text{ g}^{-1}$ (H_2O adsorption) (Torrent et al., 1994). Cu substituted hematite prepared by wet precipitation via ferrihydrite (pH 12) had a surface area of $5 \text{ m}^2 \text{ g}^{-1}$ (Cornell, unpubl.).

Hematite formed by dehydroxylation of oxide hydroxides at temperatures below 500–600 °C is porous. That formed by heating goethite *in vacuo* at 300 °C contains slit shaped meso pores which coalesce to circular macropores at temperatures $> 400 \text{ °C}$ (Naono and Fujiwara, 1980). At even higher temperatures, these pores are

Tab. 5.2 Surface areas of hematites with different morphologies

Shape	Diameter	Specific Surface Area $\text{m}^2 \text{ g}^{-1}$			Reference
		N_2	H_2O	Calculated	
Spherical	$0.107 \mu\text{m}$	12.6	16	10.8	Kandori et al., 1991
Cubic	$1.100 \mu\text{m}$	2.8	10		Kandori et al., 1991
Spherical	46 nm	15.1	–	11.4	Schudel et al., 1997
Spherical *	61 nm	27.4	–	8.5	Schudel et al., 1997
Cubic **	400 nm	16.0	9.0	–	Kandori et al., 1996

All samples were produced by forced hydrolysis of Fe^{III} solutions except for * where the sol-gel method was used.

** Grown in the presence of isopropylamine (cubic particles) or diethyltriamine (double spheres).

eliminated completely. The porosity of *solution grown* hematites appears to depend upon the morphology of the particles. The spherical particles in Table 5.2 were non porous, whereas the cubic crystals displayed inter-particle microporosity (Kandori et al., 1991). A platy hematite had a surface area of $20 \text{ m}^2 \text{ g}^{-1}$ of which 22% was pore surface area with a pore diameter of 0.5 nm (Weidler, 1995). Large, spherical hematite particles which are polycrystalline contained micropores (Kandori et al., 1996), whereas cubic and double spherical hematites prepared in the presence of various amines, were non porous.

Preparation of hematites with well defined and reproducible porosity is attracting interest because such hematites have the potential to be used in catalysis. A study using controlled rate thermal analysis (CRTA) of the dehydroxylation of goethite showed that at any particular temperature, the porosity of the hematite that resulted depended both on the rate of dehydroxylation and on the self generated water vapour pressure, i.e. whether the transformation was carried out under vacuum, in air or in a closed vessel (Perez-Maqueda et al., 1999). Hematite prepared by heating sulphated goethite (in air) at temperatures of between $350\text{--}550^\circ\text{C}$ had almost twice the surface area of hematite from non sulphated goethite (Baker et al., 2000). TEM examination showed that sulphation promoted formation of regions of mesoporous voids and stabilised these regions.

5.4.7

Magnetite

The surface area of magnetite ranges from $4 \text{ m}^2 \text{ g}^{-1}$ for Fe_3O_4 formed by reduction of hematite to close to $100 \text{ m}^2 \text{ g}^{-1}$ for particles ca. 50 nm across produced by precipitation. Mannweiler (1966) determined the surface area of a sample of cubic magnetite crystals (194 nm across) obtained by reduction of hematite, by three different methods – TEM, XRD line broadening and BET (N_2) measurement. The areas obtained by all three methods viz. $5.6\text{--}6.6 \text{ m}^2 \text{ g}^{-1}$ were in very good agreement. Partly oxidized Al-magnetite crystals grown from aqueous solution at room temperature were between 20 and 70 nm in diameter; they tended to become smaller as the structural Al increased (Schwertmann and Murad, 1990). Assuming a density of 5 g m^{-3} , a surface area of between 20 and $60 \text{ m}^2 \text{ g}^{-1}$ could be calculated. Magnetite is nonporous.

5.4.8

Maghemite

Surface areas of maghemite range from $8\text{--}130 \text{ m}^2 \text{ g}^{-1}$ depending, as usual, on the method of synthesis. Oxidation of magnetite (which may have different origins) to maghemite involves a topotactic reaction, hence the surface area of the product is close to that of its precursor. Maghemite formed from very finely divided magnetite had an area of $98 \text{ m}^2 \text{ g}^{-1}$, whereas the area of that formed by reduction of goethite via hematite to magnetite followed by oxidation was less than $20 \text{ m}^2 \text{ g}^{-1}$ (Morales et al., 1989). Maghemite formed by dehydroxylation of lepidocrocite had surface

areas ranging from 50–130 m² g⁻¹ (Giovanoli and Brutsch, 1975) and that from FeOOCH₃ had an area of ca. 60 m² g⁻¹ (Morales et al., 1989). Samples formed from hematite via magnetite by a reduction/oxidation process had length/width ratios of 1–6.3 and corresponding surface areas of 5.8–9.5 m² g⁻¹ (Morales et al., 1994).

Maghemite formed by oxidation of magnetite is non porous, whereas that obtained by dehydration of lepidocrocite is meso porous.

6

Electronic, electrical and magnetic properties and colour

6.1

Electronic properties

A detailed description of atomic and molecular theory is provided in texts by Figgis (1966), Cotton and Wilkinson (1988) and Atkins (1990). Here a brief summary of concepts and terms most relevant to the iron oxides is given.

6.1.1

Free Fe^{3+} and Fe^{2+} ions

Iron is one of the first row transition elements. The electron configuration of the Fe^{3+} ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ and for the Fe^{2+} ion it is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.

For the iron oxides, it is the Fe 3d electrons that determine the electronic, magnetic and some spectroscopic properties, hence the orbitals containing these electrons are of most interest. An orbital is the region in space occupied by a single electron or a pair of electrons; according to the Pauli exclusion principle, the maximum number of electrons in any orbital is two and where this is achieved, the electrons must have opposite spins¹⁾. There are five available d orbitals each with a different orientation in space. These are the set consisting of the d_{xy} , d_{yz} and d_{xz} orbitals which have four lobes (where electron density is a maximum) each directed between the coordinate axes of the nucleus and the second set consisting of the d_{z^2} and $d_{x^2-y^2}$ orbitals which have their lobes directed along the axes. In an isolated atom these five orbitals are degenerate, i.e. their energies are equal. In the ground state Fe^{3+} has five unpaired d electrons and Fe^{2+} has two paired and 4 unpaired electrons.

A partly filled shell²⁾ exhibits a number of *states* of different energies which arise as a result of the interactions or couplings of the electrons in the shell. These states can be determined using the Russell-Saunders coupling scheme (Hund's rules) (Figgis, 1966). A characteristic property of a state is the *spin multiplicity* which is related to the number of unpaired electrons in a shell. A singlet state has a spin multiplicity of one (two electrons of opposite spin), a doublet state has a multiplicity of two and

1) Electron spin strongly influences the magnetic properties of a compound.

2) A shell is a set of orbitals with the same principal quantum number.

so on. The ground state is the state with the lowest energy. It contains the maximum number of unpaired electrons (highest spin multiplicity) and if more than one state has the same value for net spin (S), the ground state is that with the highest net orbital angular momentum (L). In addition, the total angular momentum quantum number is $J = L + S$ if the shell is more than half-filled and $J = L - S$ if not.

The *term symbol* summarizes the properties of any state and also permits a concise representation of spectral transitions. It consists of an upper case letter ($S, P, D \dots$) to represent the net orbital angular momentum (L) and a number written as a superscript on the upper left to indicate spin multiplicity (i.e. the number of possible orientations of total spin of the atom). L is zero for Fe^{3+} (no angular momentum) and 2 for Fe^{2+} . The spin multiplicity is defined as $(2S + 1)$; $S = 5/2$ and 2 for Fe^{3+} and Fe^{2+} , respectively. The ground state term symbol for Fe^{3+} is, therefore, ${}^6S_{5/2}$ and for Fe^{2+} it is ${}^5D_4$. The subscript on the right is the value J .

6.1.2

Bound Fe ions

So far the discussion has been concerned with free ions. In a solid, however, the electrons of the Fe ions interact with those of the other ions and this leads to a change in the energy states of iron. In iron oxides and oxide-hydroxides, the cations are octahedrally and/or tetrahedrally coordinated to negatively charged $\text{O}^{2-}/\text{OH}^-$ ions (see Chap. 2) and in the electrostatic field arising from the presence of these ligands, the Fe d orbitals no longer all have the same energy. Those d electrons in orbitals directed along coordinate axes experience a greater repulsion from the negative ligands than do those whose maximum density is concentrated between the axes. As a result of this, the five d orbitals are split into two sets of different energies. The magnitude of the energy difference between the t_{2g} (d_{xy}, d_{yz}, d_{xz}) and the e_g (d_{z^2} and $d_{x^2-y^2}$) sets of orbitals is written as Δ or as $10 Dq$. On an octahedral site, the t_{2g} set has the lower energy, whereas this order is reversed on a tetrahedral site.

The d orbitals can be filled in different ways. The high spin state (HS) arises when one electron (for Fe^{3+}) occupies each orbital so that all electrons are unpaired. If, however, the energy needed to place electrons in the higher set of orbitals is greater than the electronic repulsion energy which arises when electrons are paired, two electrons may be forced into a lower orbital to give a spin paired or low spin state (LS). In iron oxides, Fe^{3+} is in the high spin state in both octahedral and tetrahedral coordination. For octahedral coordination, the ground state configuration is $(2t_g)^3 (4e_g)^2$, i.e., the first three electrons enter the t_{2g} levels and the remaining electrons the e_g level. The ground state configuration for tetrahedrally coordinated Fe^{3+} is $(e_g)^2 (t_{2g})^3$.

For octahedral coordination, the t_{2g} state is stabilized by energy equivalent to $2/5 \Delta$ (Δ is of the order of 10000 cm^{-1} to 20000 cm^{-1}) and the e_g state is destabilized by $3/5 \Delta$. The stabilization energy is termed the crystal field stabilization energy (CFSE) and for Fe^{3+} is 0 for HS_{oct} and 2Δ for both HS_{tet} and LS_{oct} coordination. For Fe^{2+} , it is $2/5 \Delta$, $12/5 \Delta$ and $3/5 \Delta$ for HS_{oct} , LS_{oct} and HS_{tet} , respectively. This energy influences various thermodynamic and other properties of the compounds (Figgis,

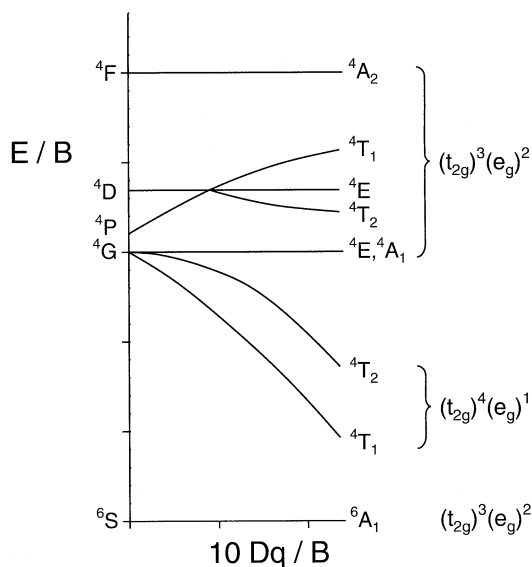


Fig. 6.1 Tanabe-Sugano diagram for high spin Fe^{III} in either octahedral or tetrahedral coordination (Sherman, 1985, with permission).

1966). For example, the inverse spinel structure of magnetite (see Chap. 2) results from the fact that the CFSE of Fe^{2+} is greater for octahedral than for tetrahedral coordination, so Fe^{2+} preferentially occupies octahedral sites. For Fe^{3+} the CFSE is zero for both octahedral and tetrahedral coordination, so that this ion has no preference for either type of coordination.

In the same way that the set of five d orbitals is split by the electrostatic field of the surrounding ligands so also can the various multi-electronic states (multiplets) arising from Russell-Saunders coupling be split into several components by the exchange energy, i.e. exchange coupling. The energies of the different multiplet states which arise as a result of the ligand (or crystal) field splitting can be represented as a function of crystal field stabilization energy in a Tanabe-Sugano diagram (Fig. 6.1). Such a diagram is used to predict electronic transitions between different states and to assist in the interpretation of optical spectra (Sherman & Waite, 1985). In the multiplet environment, the term symbol¹⁾ for Fe^{3+} in the ground state and on an octahedral or a tetrahedral site, is ${}^6A_{1g}$.

6.1.3

Molecular orbital description of bonding in iron oxides

Interactions between Fe and the oxide ions in the iron oxides have been described using the molecular orbital method. This approach regards the electrons as being subject to the influence of all the nuclei in the entity under consideration. The mole-

1) The letters used to designate the single and multielectronic states are obtained using group theory (Figgis, 1966).

cular orbitals are constructed by the linear combination of the appropriate atomic orbitals, i.e. only orbitals with the appropriate symmetry can interact. In iron oxides, the Fe 3d electrons are, to a large extent, localized on the Fe atom and its immediate coordination site. The electronic structures of these compounds can, therefore, be described in terms of the molecular energy levels of simple atomic clusters that represent a basic structural entity similar to that in the solid, i.e. FeO_6^{9-} for Fe^{3+} in octahedral coordination (e.g. in hematite), FeO_6^{10-} for Fe^{2+} in octahedral coordination (e.g. in wüstite) and FeO_4^{5-} for tetrahedrally coordinated Fe^{3+} (e.g. in magnetite). These energy levels were first calculated by Tossell et al. (1974) using the self consistent Xa scattered wave (SCF-XaSW) method and later extended by Tossell (1978), Maruthe and Trautwein (1983) and Sherman and Waite (1985). Figure 6.2 shows the Fe-O bonding energy levels for the FeO_6^{9-} and the FeO_4^{5-} cluster. Orbitals with similar character and energy are grouped into bands. The energy levels which determine most of the properties of the iron oxides are the Fe 3d crystal field bands which are partly filled and the 2p orbitals of the ligands. All the iron oxides possess a significant degree of covalent bonding (Sherman, 1985). The trigonal distortion of the octahedral coordination in the hematite structure (see Chap. 2) lowers the symmetry of the FeO_6^{9-} cluster; the electronic structures of the distorted and undistorted clusters are, however, very similar (Sherman, 1985).

These three types of clusters all involve one electron orbital. They provide a basis for the description of the d-d (i.e. ligand field) transitions and the ligand to metal charge transfer transitions which are responsible for most of the UV-visible spectra and opti-

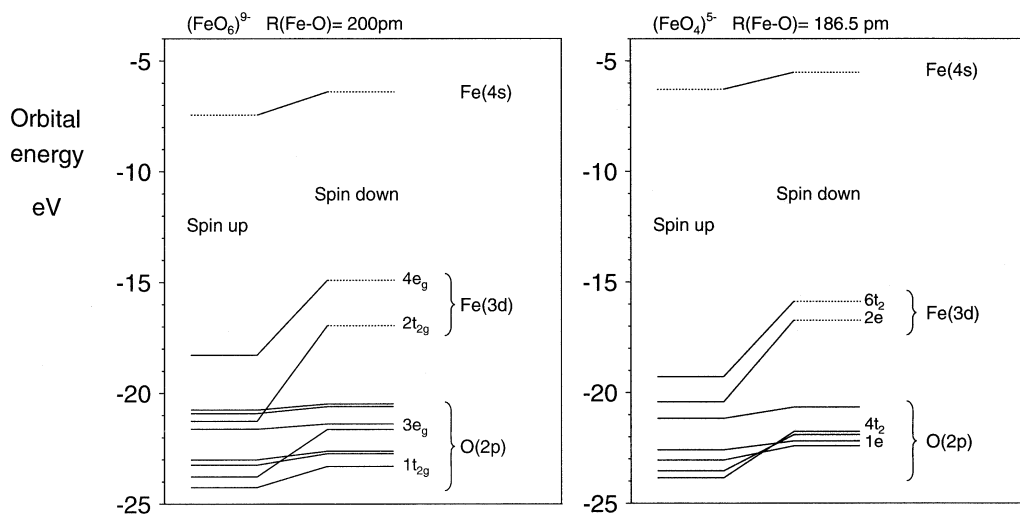


Fig. 6.2 Molecular orbital diagram for an FeO_6^{9-} cluster similar to that found in hematite (left) and an FeO_4^{5-} cluster (right). The most important Fe-O bonding and antibonding orbitals are labelled. The remaining orbitals ($6a_{1g}$, $5t_{1u}$, $6t_{1u}$, $1t_{2u}$ and $1t_{1g}$) are mainly non bonding. The orbitals indicated by dashed lines are unoccupied (Sherman, 1990, with permission).

cal properties of the iron oxides (see Chap. 7). For interpretation of spectra, these one electron orbital energies calculated for the cluster must be related to the multi-electronic states found in the actual oxides (Sherman, 1985; Sherman & Waite, 1985).

6.2

Electrical properties

Hematite, wüstite, maghemite and magnetite are semiconductors; magnetite displays almost metallic properties. For a compound to be a semiconductor, the essential characteristic is that the separation between the valence band of orbitals and the conduction band is less than 5 eV; this condition is met for the above oxides. In a semiconductor the Fermi level (i.e. the level below which all electron energy levels are filled) lies somewhere between the valence band and the conduction band.

Electrical conductivity is due to the motion of free charge carriers in the solid. These may be either electrons (in the empty conduction band) or holes (vacancies) in the normally full valence band. In a p type semiconductor, conductivity is mainly via holes, whereas in an n type semiconductor it involves electrons. Mobile electrons are the result of either intrinsic non-stoichiometry or the presence of a dopant in the structure. To promote electrons across the band gap into the conduction band, an energy greater than that of the band gap is needed. Where the band gap is small, thermal excitation is sufficient to achieve this. In the case of most iron oxides with semiconductor properties, electron excitation is achieved by irradiation with visible light of the appropriate wavelength¹⁾ (photoconductivity).

Light absorption causes formation of an electron/hole (e^-h^+) pair in the interfacial region of the solid and, in the presence of an electric field (e.g. when the solid is held in an electrolyte), the electrons migrate inwards towards the bulk of the solid and the holes move towards the surface and react with the FeOH groups, i.e. the charges separate. The surface reaction is, $Fe-OH + h_{VB}^+ \rightarrow Fe(OH)_s^+$ where s = surface and h_{VB}^+ is a hole. A feature of the iron oxides is electron/hole pair recombination – many electrons recombine with the holes and are neutralized – which decreases the photo-activity of the solid. The extent of recombination depends to some extent on the pH of the solution and its effect on the proportion of FeOH groups at the surface (see Chap. 10 and Zhang et al., 1993).

At the semiconductor/solution interface the electronic charge is redistributed; at equilibrium an n type semiconductor develops a positive charge and the solution a negative one; the situation is analogous to the electrical double layer which forms as a result of redistribution of ions between the solid and the electrolyte (see Chap. 10). The bulk solid electrochemical potential in a semiconductor is separated from that at the interface by a space charge region in the solid adjacent to the surface where the excess charge is localized (Fig. 6.3). In this region the energy band gaps are influenced (“bent”) by the potential at the solid/solution interface (White, 1990). When there is no excess charge held in the surface state, the potential in the space charge

1) 1 eV = 1000 cm⁻¹.

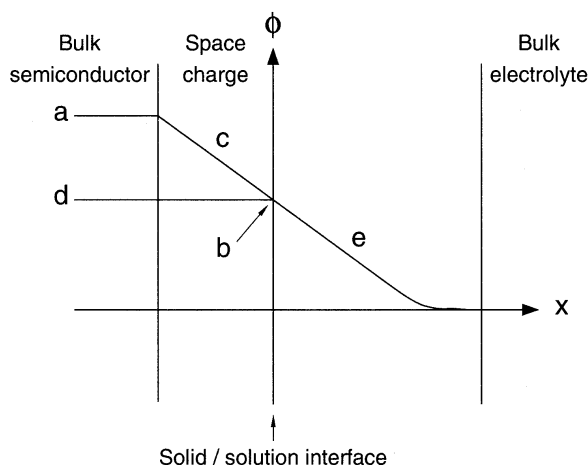


Fig. 6.3 Schematic picture of the electrochemical potential ϕ as a function of distance x in an oxide semiconductor electrolyte system: a) bulk semiconductor potential; b) solid/solution interface potential; c) space charge potential; d) flat band potential; e) potential in the double layer (White, 1990, with permission).

region is constant and equal to that of the bulk semiconductor; this is the rest or flat band potential and corresponds to the point of zero charge in the electrical double layer (White, 1990). The more negative the flat band potential, the greater the band bending and the greater the efficiency of the semiconductor (Quinn et al., 1976).

The photocatalytic activity of iron oxides with semiconductor properties is of two kinds. The holes at the solid surface can oxidize either adsorbed or solution species (see Chap. 11), or both holes and electrons may induce dissolution of the solid phase (see Chap. 12).

6.2.1

Semiconductor properties of iron oxides

Stoichiometric *hematite* is an n type semiconductor. The conduction band is composed of empty Fe^{3+} d orbitals and the valence band consists of full $2t_{2g}$ Fe 3 d ligand field orbitals with some admixture from the oxygen antibonding 2p orbitals (Fig. 6.4). Despite intensive investigations, there is still controversy concerning the semiconductor properties of hematite. Although the band gap is commonly considered to be 2.2 eV, Sherman (1990) has suggested that it corresponds to an $\text{O}^{2-}-\text{Fe}^{3+}$ charge transfer transition with an energy of 4.7 eV. In such a case hematite should not be highly photoreactive under the influence of solar radiation; Sherman (1990) suggested that photoactivity is induced by visible light associated with the tail of the $\text{O}^{2-}-\text{Fe}^{3+}$ charge transfer band. The flat band potential was found by Dare-Edwards et al. (1983) to be -0.5 V vs. SCE (standard calomel electrode) in M NaOH; the value of this potential is pH dependent. A possible cause of the uncertainty concerning the semiconductor properties is their strong dependence on both the thickness of the sample and the surface properties; the latter are strongly influenced by pretreatment which can convert some hematite to surface magnetite (Dare-Edwards et al., 1983; Gleitzer et al., 1991).

Calculation of the electronic structure of freshly cleaved hematite surfaces suggest that the local electronic structure of the surface may be very different from the bulk

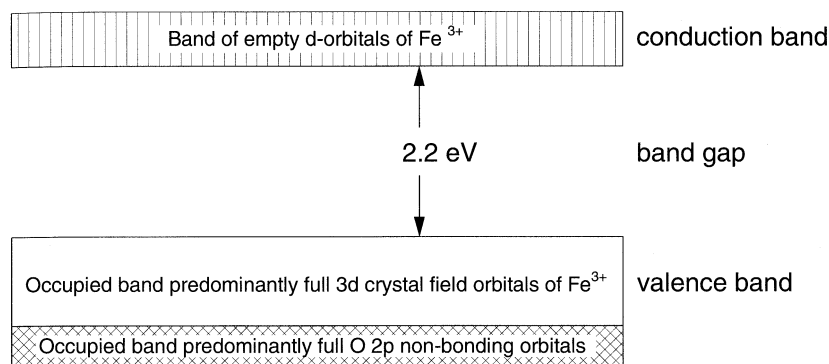


Fig. 6.4 Band structure of hematite (Zhang et al., 1993, with permission).

properties (Becker et al. 1996). Hematite has a very low hole mobility (room temperature) of $\sim 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Leland & Bard, 1987).

Certain properties of hematite – its stability against dissolution at $\text{pH} > 4$ and the fact that a reasonable amount (29%) of visible light has energies greater than the (accepted) hematite band gap (2.2 eV) have prompted investigations into use of this oxide as an anode for the photoassisted electrolysis of water for hydrogen production (Quinn et al., 1976; Hardee & Bard, 1978; Kennedy & Reese, 1978; Kiwi & Grätzel, 1987). In these investigations, the hematite anodes were in the form of thin films or single crystals. The quantum efficiency of the pure hematite electrodes was found to be low and a further disadvantage was the high resistivity of hematite. Thin films consisting of oriented needles of hematite (0.5 μm length) on a conducting glass substrate were found to have better photo-current efficiency than thin films of sintered hematite particles. The incident photon to current conversion efficiency doubled as the pH of the electrolyte was increased from 6.8 to 12.0 (Beermann et al. 2000). The photoelectronic properties of hematite have been improved by doping with Nb or Ge (Somorjai & Salmeron, 1986).

Magnetite can be slightly metal deficient with vacancies on the octahedral sites. It is both an n and a p type semiconductor. The band gap is small (0.1 eV), hence magnetite has the lowest resistivity of any oxide. The conductivity of $10^2\text{--}10^3 \Omega^{-1} \text{ cm}^{-1}$ is almost metallic. In edge sharing octahedra, the Fe^{2+} and Fe^{3+} ions on the octahedral sites are close together and as a result, the holes can migrate easily from Fe^{2+} to Fe^{3+} and this accounts for the good conductivity. *Maghemite* is an n type semiconductor (band gap 2.03 eV) and *wüstite* a p type semiconductor (band gap 2.3 eV).

Band gaps for goethite, lepidocrocite, akaganéite and $\delta\text{-FeOOH}$ are 2.10 eV, 2.06 eV, 2.12 eV and 1.94 eV, respectively. The conductivity of these materials is very low at room temperature (ca. $10^{-9} \Omega^{-1} \text{ cm}^{-1}$) and increases somewhat as the sample is heated to ca. 140°C (Kaneko & Inouye, 1974). The heat treatment partly dehydrates the surface and this was considered to produce some Fe^{2+} leading to hopping of electrons between Fe^{2+} and Fe^{3+} (Kaneko & Inouye, 1976, 1976a).

6.3

Magnetic properties

6.3.1

Basic definitions

Important parameters used to characterize the magnetic properties of solids are the magnetic susceptibility, the permeability and the magnetic moment (Cotton & Wilkinson, 1988; West, 1988).

When a substance is placed in a magnetic field of strength, H (units Tesla), the intensity of magnetization J (i.e. the *magnetic moment* of the sample per unit volume, [$A\ m^{-1}$ or $J\ T^{-1}\ m^{-3}$]), is related to H by the *magnetic susceptibility*, κ , of the substance,

$$J = \kappa H \quad (6.1)$$

Magnetic susceptibility can be expressed in terms of volume, as κ ($m^3\ m^{-3}$ or $J\ T^{-2}\ m^{-3}$), or mass, χ ($m^3\ kg^{-1}$ or $J\ T^{-2}\ kg^{-1}$).

The density (or flux) of the lines of force in a solid placed in a magnetic field (H) is termed the *magnetic induction*, B , and is given by the relationship,

$$B = \mu (H + J) \quad (6.2)$$

The tendency of the magnetic lines of force to pass through a medium relative to their tendency to pass through a vacuum is the *magnetic permeability*, μ . This is one of the parameters that distinguishes a diamagnetic material from a paramagnetic substance. Permeability is defined as,

$$\mu = \mu_0 (1 + \kappa) \quad (6.3)$$

where μ_0 is the vacuum permeability.

The magnetic moment, m , is a term used to quantify the magnetic properties of a substance. It is not measured directly, but is obtained from the measured molar susceptibility to which it is related, i.e.

$$\chi = \mu_0 \frac{Nm^2}{3kT} \quad (6.4)$$

where N is the Avogadro number and k is the Boltzmann constant. The fundamental magnetic moment is the Bohr magneton, β , i.e.

$$\beta = \frac{eh}{4\pi m_e c} = 9.2732 \cdot 10^{-24}\ Am^2 \quad (6.5)$$

where e and m_e are the charge and mass of the electron, respectively. Expression (6.4) which relates magnetic moment to susceptibility, can be reduced to

$$m = 2.83 \sqrt{\chi T} \quad (6.6)$$

The units of magnetic moment are Joule/Tesla, but this parameter is often expressed in Bohr magnetons.

The magnetic moment arises as a result of interactions between the spin moment of the electron, μ_s , and the orbital moment; the contribution of the orbital moment is of comparatively minor importance. The magnitude of the overall spin moment depends upon the number of unpaired electrons in the atom, i.e.

$$\mu_s = g \sqrt{S(S+1)} \quad (6.7)$$

S is the sum of the spin quantum numbers, to which each electron contributes $\pm 1/2$ and g is the gyromagnetic ratio, i.e. the ratio of the magnetic moment to the angular momentum. For a free electron, $g = 2$.

For high spin Fe^{3+} with five unpaired d electrons and zero orbital angular momentum, both the calculated and measured magnetic moments are 5.9 Bohr magnetons (BM). The measured magnetic moment of Fe^{2+} of 5.1 to 5.5 BM is, however, higher than the calculated value of 4.9 BM owing to a contribution from the orbital moment of the ion.

6.3.2

Types of magnetism (Fig. 6.5)

Diamagnetism is a basic property of all substances and involves a slight repulsion by a magnetic field. The magnetic susceptibility of a diamagnetic substance is small (-10^{-6}), negative and independent of temperature. Iron oxides display additional types of magnetism.

Paramagnetic substances are attracted towards a magnetic field. Such substances possess unpaired electrons which are randomly oriented on different atoms. Each atom, ion or molecule of a paramagnetic substance can be visualized as a small magnet with its own, inherent magnetic moment. Application of a magnetic field causes (partial) alignment of these magnets parallel to the field. The magnetic susceptibility is positive and small (0 to 0.01). It varies with temperature and its behaviour is described by the Curie-Weiss law,

$$\chi_M = \frac{C_M}{T - T_C} \quad (6.8)$$

C_M and T_C are the Curie constant and the Curie temperature, respectively and T is the temperature. The temperature dependence of χ_M is the result of two opposing tendencies; as the temperature rises, the increased alignment of the magnetic moments in the substance is opposed by the stronger thermal vibrations, hence χ_M decreases. Below a certain temperature (Néel or Curie) which depends on the oxide itself, iron oxides undergo a transition to a magnetically ordered state and become ferromagnetic, antiferromagnetic, ferrimagnetic or speromagnetic. The transition tem-

perature is termed the Curie temperature (T_C) for ferromagnetic and ferrimagnetic substances and the Néel temperature (T_N) for antiferromagnetic substances.

Ferro- and ferrimagnetic substances are strongly attracted by a magnetic field. They contain unpaired electrons whose moments are, as a result of interactions between neighbouring spins, at least partly aligned even in the absence of a magnetic field. The spin coupling energy is positive.

In a *ferromagnetic* substance, the alignment of the electron spins is parallel (Fig. 6.5a). Such substances have an overall *net* magnetic moment, a large magnetic permeability and a large, positive susceptibility (0.01 – 10^6). With rising temperature, the ordered arrangement of the spins decreases owing to thermal fluctuations of the individual magnetic moments and the susceptibility falls rapidly. The temperature dependence of the susceptibility does not follow the Curie-Weiss law.

In an *antiferromagnetic* substance, the electron spins are of equal magnetic moment and are aligned in an antiparallel manner (Fig. 6.5b). Such substances have zero overall magnetic moment, a positive permeability and a small positive susceptibility (0 – 0.1). Increasing the temperature usually causes susceptibility to increase because the antiparallel ordering is disrupted.

Ferrimagnetic substances consist, like antiferromagnetic materials of at least two interpenetrating sublattices and the alignment of spins is, again, antiparallel. In a ferrimagnetic substance, however, the different spins have unequal moments, so that a ferrimagnetic material has a net magnetic moment (Fig. 6.5c).

Ferromagnetic, antiferromagnetic and ferrimagnetic substances have a domain structure: only the particles in a range from 50 to 500 nm in size consist of a single domain. The spins within a domain are either parallel or antiparallel, but the different domains have different spin orientations. To eliminate the domains in a ferro- or antiferromagnetic substance a sufficiently high magnetic field must be applied; as the applied magnetic field is increased, the spins in the domains become increasingly aligned. At a high enough magnetic field, saturation magnetization is reached, i.e. the spins of all the domains are parallel.

A plot of magnetization against an applied magnetic field displays a hysteresis loop, the two branches of which correspond to the magnetization and demagnetiza-

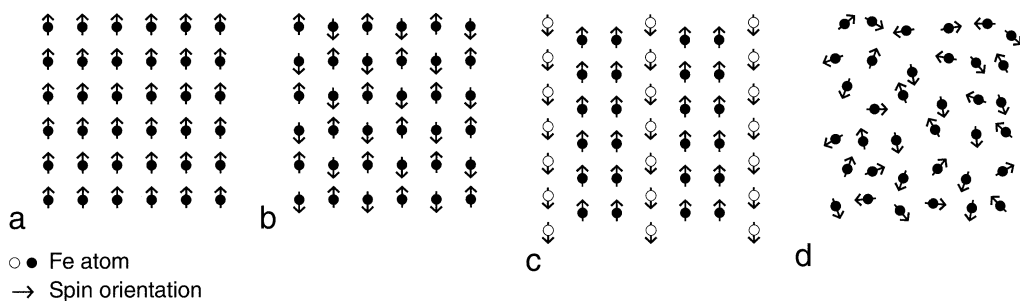


Fig. 6.5 Schematic illustration of the main varieties of magnetic order: a) ferromagnetism, b) antiferromagnetism, c) ferrimagnetism, d) speromagnetism (Coey, 1988, with permission).

tion processes. The magnitude of the reverse field required to demagnetize a ferro- or ferrimagnetic substance is termed the *coercivity*. Magnets with low coercivity are termed “soft”. “Hard” magnets have both a high coercivity and a high remanent magnetization,¹⁾ hence they are not easily demagnetized. Materials used in magnetic recording devices have coercivities ranging from 5.02 to 18.65 Am⁻¹.

Super-paramagnetism arises as a result of magnetic anisotropy, i.e. the existence of preferred crystallographic directions along which the electron spins are most readily aligned and the substance most easily magnetized. The preferred direction for easy magnetization is along some crystallographic axis or set of axes, e.g. for magnetite, along the [111] directions. If sufficient energy is supplied, magnetism can be reversed along these axes. The time required for spin reversal, the relaxation time, τ depends on the height of the energy barrier between the forward and reverse spin states and the temperature, according to

$$\tau \propto \exp\left(\frac{K_{\text{eff}} \cdot V}{kT}\right) \quad (6.9)$$

The height of the energy barrier between the forward and reverse states is the product of the particle volume, V , and the anisotropy constant K_{eff} (which is, to some extent, a function of particle size). Superparamagnetic relaxation occurs when the thermal energy of the particles exceeds the activation energy barrier between the spin states and so allows rapid, spontaneous fluctuations between these states. The effect of these spin reversals is that the observed magnetic field is reduced or even absent.

Because the appearance of the superparamagnetic effect depends on the particle size and on the anisotropy constant, it is often displayed at room temperature by iron oxides <10 nm in size, for example, soil iron oxides. Superparamagnetic relaxation may be counteracted by lowering the temperature and thereby increasing τ . Superparamagnetic particles will usually be ordered below a blocking temperature, T_B , which is:

$$T_B = \frac{K_{\text{eff}} \cdot V}{25 k} \quad (6.10)$$

Speromagnetism (Fig. 6.5 d) is a property of some amorphous or poorly ordered materials containing metal-O-metal bonds which, if the metal carries a magnetic moment, can support super-exchange reactions (Coe & Readman, 1973).

6.3.3

Magnetic behaviour of iron oxides

Most of the data for this section came from Murad and Johnston (1987), Murad (1988) and Coey (1988). The main type of magnetic interaction between Fe ions on adjacent sites in a solid is the electrostatic exchange interaction; this tends to cause

1) Remanent magnetization is the magnetization that remains after the magnetic field has been switched off.

Tab. 6.1 Exchange interactions in iron oxides (Coe, 1988; with permission)

<i>Ion pair</i>	<i>Fe-O-Fe bond angle</i>	<i>Type of interaction</i>
$\text{Fe}^{3+}\text{-Fe}^{3+}$	90°	weak antiferromagnetic
	120°	strong antiferromagnetic
$\text{Fe}^{2+}\text{-Fe}^{2+}$	90°	weak antiferromagnetic
	$120\text{--}180^\circ$	strong antiferromagnetic

parallel or antiparallel alignment of the spins. In iron oxides, the Fe^{3+} ions are surrounded by O^{2-} or OH^- ions, so the exchange reactions proceed via the intervening ligand. This process is termed *super-exchange*. Unpaired electrons in the e_g orbitals of the Fe^{3+} ions interact magnetically with electrons on the p orbitals of the O^{2-} ions and, provided the cation and the ligand are close enough to permit coupling of their electrons, a chain coupling effect which passes through the crystal (percolation), takes place. The exchange constants for these processes have been measured and found to depend on the Fe-O bond length and, above all, on the bond angle. Exchange interactions are strong when the Fe^{3+} bond angles are $120\text{--}180^\circ$ and much weaker when these angles are 90° as is the case where FeO_6 octahedra share faces (Coe, 1988). The types of exchange reactions in iron oxides are listed in Table 6.1. Super-exchange interactions in Fe^{2+} oxides show a similar dependence on bond angle. Where Fe^{2+} and Fe^{3+} are present together, as in magnetite, electron delocalization between Fe^{2+} and Fe^{3+} on an adjacent site, can occur.

The magnetic properties of iron oxides can be determined using Mössbauer spectroscopy, neutron powder diffraction and magnetometry (see Chap. 7). The characteristic parameters are the magnetic moment, the permeability, the saturation magnetization, the magnetic anisotropy constants and the B_{hf} (Tab. 6.2).

The origin of the magnetic hyperfine field (B_{hf}) in iron oxides is the polarization of the inner s electrons by the atom's own 3d electrons. Minor contributions also come from the polarization of the s electrons by the 3d electrons of neighbouring cations and from the spin dipolar moment of the 3d electrons themselves. Below T_N or T_C , iron oxides undergo spontaneous magnetization. The B_{hf} increases rapidly as the temperature falls below that of the ordering temperature and at low enough temperatures approaches the saturation value, i.e. the maximum value obtainable at 0 K. The magnitude of the saturation hyperfine field can provide an estimate of the degree of covalent character in the solid (Murad & Johnston, 1987). B_{hf} decreases as diamagnetic cations, such as Al, enter the structure. This can be explained on the basis of a supertransfer mechanism: as the number of Al-O-Fe paths increases, the supertransfer of 3d-spin density into the outer s shell of the iron nuclei, and, hence, the total hyperfine field, decreases (De Grave et al., 1995). The decrease in B_{hf} for the various Fe oxides is around $3\text{--}4\text{ T per }10^{-2}\text{ Al}/(\text{Fe}+\text{Al})$ (De Grave et al., 1982; Murad & Schwertmann, 1983; Bowen et al., 1994).

Tab. 6.2 Magnetic properties of the iron oxides (data from Coey, 1988, and Soffel, 1991; with permission)

Oxide	Temperature [§]	Magnetic structure	Saturation Magnetization σ_s at 300 K $\text{Am}^2 \text{kg}^{-1}$ [§]	Anisotropy Constant K_{eff} Jm^{-3}	Magneto- Restriction Constant λ	Magnetic hyperfine field	
	K					B_{hf} 295 K	4 K
Goethite	400 T _N	antiferromagnetic	0.01–1	10 ³	–	38.2	50.6
Lepidocrocite	77 T _N	antiferromagnetic	–	–	–	–	46
Akaganéite	290 T _N	antiferromagnetic	–	–	–	–	48.2
δ-FeOOH	440–460 T _N	ferrimagnetic	7–20	–	–	–	–
Feroxyhyte	455 T _C	ferrimagnetic	–	–	–	–	59
HP FeOOH	470 T _N	antiferromagnetic	–	–	–	–	–
Ferrihydrite	~ 350 T _N *	speromagnetic	–	10 ⁵	–	–	47–50
Bernalite ^{c)}	~ 427 T _N	weakly ferromagnetic	–	–	–	43.1	~ 56.0
Hematite	956 T _C	weakly ferromagnetic	0.3	1–6 · 10 ⁴	8 · 10 ⁻⁶	51.8	54.2
Magnetite	260 T _M	antiferromagnetic	–	–	–	–	–
	850 T _C	ferrimagnetic	92–100	10 ⁴ –10 ⁵	35 · 10 ⁻⁶	–	–
	120 Verwey transition	–	–	–	–	–	–
Maghemite	820–986 T _C	ferrimagnetic	60–80	10 ⁵	35 · 10 ⁻⁶	50	52.6
ε-Fe ₂ O ₃	1026 T _N	antiferromagnetic	–	–	–	–	–
Fe(OH) ₂	34 T _N	planar antiferro- magnetic	–	–	–	–	–
Wüstite	203–211 T _N	antiferromagnetic	–	–	–	–	–

§ T_N: Néel temperature; T_C: Curie temperature; T_M: temperature of Morin transition

§ Am² kg⁻¹ is identical to J T⁻¹ kg⁻¹; c) McCammon et al. 1995; De Grave et al. 1999; * 2-line; Seehra et al. 2000

6.3.4

The different iron oxides

6.3.4.1 Goethite

Goethite has a Neel temperature of 400K (De Grave & Vandenberghe, 1986), and is therefore antiferromagnetically ordered at room temperature. The ordering behaviour of goethite is influenced by its comparatively low anisotropy constant (10⁻³ Jm⁻³) and by particle size and the extent of aluminium substitution; B_{hf} is particularly sensitive to the latter properties because T_N is so close to room temperature. An equation for the decrease in B_{hf} when both Al substitution and crystallinity vary is shown in Chapter 3. A similar dependence of B_{hf} on Al substitution is also found for soil goethites (Friedl & Schwertmann, unpubl.). Substitution of Al in the goethite structure also reduces T_N; as Al/(Fe + Al) increased from 0 to 0.3, T_N dropped from 390 to 210 K (Fleisch et al., 1980).

In the antiferromagnetic state, the spins are oriented along the *b*-axis with up and down spins in alternate chains of octahedra (Fig. 6.6). The strongest exchange interaction is between corner sharing octahedra in continuous chains where the Fe₁-O-Fe₂ bond angle is 124°. Super-exchange interactions between edge sharing octahedra (i.e. within the double chains) are weak owing to the lower bond angle involved.

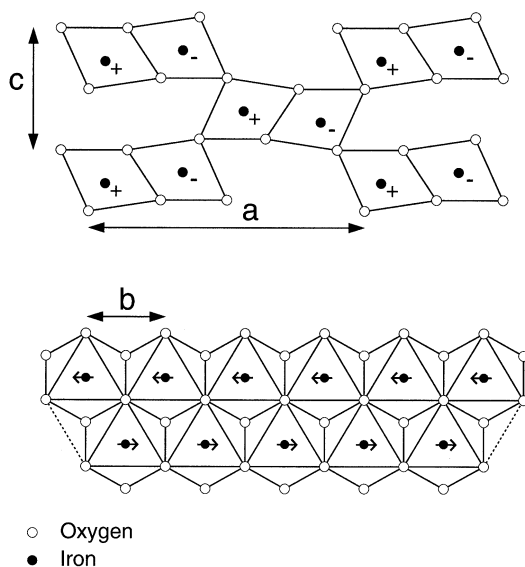


Fig. 6.6 Crystal and magnetic structure of goethite (Coey, 1988, with permission).

Neutron diffraction showed that the magnetic and crystallographic unit cells are the same (Forsyth et al., 1968). Particles smaller than 15–20 nm (e.g. soil goethites) display super-paramagnetism at room temperature and particles smaller than 8 nm are super-paramagnetic down to 77 K (Janot et al. 1973). The super-paramagnetic behaviour of microcrystalline goethite has been attributed both to a reduced magnetic coupling between the crystallites (Mørup & Tronc, 1994) and to a relatively high concentration of vacancy defects (Boquet et al., 1990).

6.3.4.2 Lepidocrocite

Lepidocrocite is paramagnetic at room temperature. The Néel temperature of 77 K is much lower than that of the other iron oxides and is the result of the layer-like structure of this mineral. The sheets of $\text{Fe}(\text{O}, \text{OH})_6$ octahedra are linked by weak hydrogen bonds, hence magnetic interactions are relatively weak. The saturation hyperfine field is also lower than for any other iron oxide (Tab. 6.2). In the antiferromagnetic state, the spins are ordered parallel to the *c*-axis with spins in alternate layers having opposite signs. A decrease of T_N by 5 K was observed for Al-lepidocrocites with an $\text{Al}/(\text{Fe} + \text{Al})$ ratio of 0.1 (De Grave et al., 1995).

6.3.4.3 Akaganéite

At room temperature, akaganéite is, like lepidocrocite, paramagnetic. It becomes antiferromagnetic below the Néel temperature of 290 K (Murad, 1988). The value of T_N and the strength of the magnetic interactions are variable and depend upon synthesis conditions (i.e. the temperature and the length of the hydrolysis period). These influence the amount of interstitial water in the compound, which in turn induces spin reduction. T_N decreases linearly to 250 K as the $\text{H}_2\text{O}/\text{unit cell}$ rises to $0.02 \text{ mol mol}^{-1}$ (Chambaere & De Grave, 1984a).

In the antiferromagnetic state, the spins are oriented parallel to the *c*-axis. Mössbauer studies have indicated that the number and type of subsites in the magnetic structure may be influenced by the halide concentration, the nature of the halide and the level of excess protons which balance the halide charge. When chloride is present in the structure, there are two different Fe^{3+} sites, whereas for fluoride-containing akaganéite, the number of non-equivalent cation sites may be greater.

6.3.4.4 δ -FeOOH, feroxyhyte and high pressure FeOOH

Synthetic δ -FeOOH is ferrimagnetic at room temperature. The Néel temperature has been estimated as being at around 440–460 K; it has not been determined directly owing to the conversion of δ -FeOOH to hematite at 100–150 °C. The magnetic structure is basically antiferromagnetic with the magnetic moments being parallel to the *c*-axis. Ordering of the vacancies on alternate planes is the cause of the ferrimagnetism which can be made to disappear by heating the sample. Low-temperature Mössbauer studies have shown that there are two different Fe sites in the structure, but it has not been established whether these are two different octahedral sites or both octahedral and tetrahedral sites.

Owing to its small particle size and poor crystallinity, the mineral feroxyhyte (δ' -FeOOH) is superparamagnetic at room temperature. Superparamagnetic relaxation is also observed for small particles of the synthetic compound, which had a B_{hf} at 4.2 K of 51.3 T (Carlson & Schwertmann, 1980).

The high pressure form of FeOOH is more compact than any other iron oxide hydroxide, hence it has a higher than usual Néel temperature of 470 K. At room temperature, high pressure FeOOH is antiferromagnetic with a collinear spin arrangement parallel to the *c*-axis (Pernet et al., 1973). High-pressure FeOOH is completely miscible with CrOOH. Substitution with Cr reduces T_N to the extent that with 80% Cr substitution, there is no magnetic ordering even at 91 K.

6.3.4.5 Ferrihydrite

Magnetic ordering of ferrihydrite takes place over a range of temperatures and these temperatures are low to very low (Murad & Johnston, 1987). This behaviour is the result of the small size of the ferrihydrite particles and their comparatively wide size distribution. A range of blocking temperatures defined as the temperature at which 50% of the Mössbauer spectrum is magnetically split has been reported for different samples of natural and synthetic ferrihydrite depending on both the source and degree of ordering (6- or 2-line, see Chap. 2) of the material (Murad & Johnston, 1987; Murad, 1988; Coey, 1988). At room temperature ferrihydrite is superparamagnetic. The blocking temperature of various ferrihydrites was found to range between 115 and 25 K. At 4.2 K the spectra of all ferrihydrite samples have been found to be magnetically split and superparamagnetic ordering in which the spins freeze into a random, non-collinear structure is adopted (Coey & Readman, 1973). The anisotropy constant is around 10^5 J m^{-3} (Murad & Johnston, 1987). Recently, a Néel temperature for 2-line ferrihydrite of $\sim 350 \text{ K}$ was derived from neutron scattering data (Seehra et al. 2000).

6.3.4.6 Hematite

Hematite is paramagnetic above 956 K (T_C). At room temperature it is weakly ferromagnetic and at 260 K (the Morin temperature, T_M), it undergoes a phase transition to an antiferromagnetic state. Particles smaller than about 8 nm display superparamagnetic relaxation at room temperature. A plot of the dependence of the B_{hf} (H_i) of hematite on temperature is shown in Figure 6.7: the plot follows an approximate Brillouin curve.

The spin structures of hematite are shown in Figure 6.8. Above T_M , the Fe^{3+} ions are antiferromagnetically coupled across the shared octahedral faces along the c -axis.

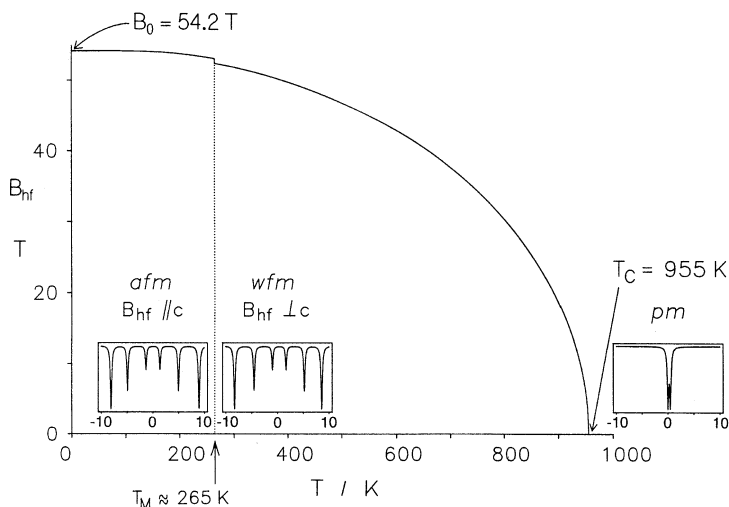


Fig. 6.7 Temperature dependence of the magnetic properties of hematite. T_C = Curie temperature, T_M = Morin temperature, pm = paramagnetic region, wfm = weakly ferromagnetic region; afm = antiferromagnetic region. The insets show simulated Mössbauer spectra of hematite in the paramagnetic, weakly ferromagnetic and antiferromagnetic states (Murad, 1988, with permission).

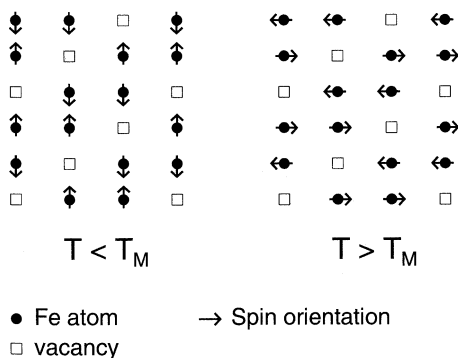


Fig. 6.8 Spin ordering in hematite above and below T_M (Coe, 1988, with permission).

In the basal plane, there are two interpenetrating antiferromagnetic sublattices. As the electron spins of these sublattices are not exactly antiparallel, (i.e. spin canted) with a canting angle of $<0.1^\circ$, a weak ferromagnetic interaction results. At $T > T_M$ (e.g. room temperature), this effect dominates the magnetic behaviour. At T_M , competition between the weak magnet-anisotropy of the Fe^{3+} ion and the dipolar anisotropy causes the electron spins to reorientate from the basal plane at $T > T_M$ to an angle of 7° to the c -axis at $T < T_M$ (Morrish et al., 1963; Artman et al., 1965). In this state, the spins are exactly antiparallel and hematite is antiferromagnetic.

Where pairs of FeO_6 octahedra share faces (along the c -axis), the Fe^{3+} ion in each octahedron of the pair can be regarded as being sandwiched between two triplets of O^{2-} ions or alternatively that a triplet of O^{2-} ions separates the Fe^{3+} in the two octahedra. The Fe^{3+} ions in the $\text{Fe-O}_3\text{-Fe}$ units have opposite spins. Weak super-exchange interactions take place between these Fe^{3+} ions (antiferromagnetically coupled), whereas stronger interactions (ferromagnetic coupling) exist between ions in the corner sharing octahedra where the Fe-O-Fe bond angle is large. Exchange constants for the different Fe-O-Fe pairs are listed in Table 6.3.

The magnetic behaviour of hematite depends on crystallinity/particle size and on the extent of cation substitution. Both poor crystallinity and substitution of cations, except for Rh, (Coe & Sawatzky, 1971) reduce B_{hf} and T_M ; substitution also lowers T_C (Murad, 1988). For example, T_M was found to increase linearly with $1/d$ (d = crystal size) from 233 to 261 K as d increased from 0.070 to 0.620 μm : $T_M = 264.2 - 2.194/d$ (Amin & Arais, 1987). This relationship, however, depends on the way the hematite was formed (Vandenberghe et al. 2000) (Fig. 6.9 right). In contrast, according to Dang et al. (1998), the T_M of pure hematite is determined by its unit cell parameters a and c (which in turn depend on the OH content) and not on particle size. A hematite with a particle size of 16 ± 3 nm was superparamagnetic down to 230 K, had a magnetic blocking temperature of 143 ± 5 K and was weakly ferromagnetic at least down to 5 K (Bødker et al. 2000).

Among the cations having an effect on T_M are Al, Ga, Cr, In, Mn, Sn and Ti (Flanders & Remeika, 1964; De Grave et al., 1982; Vandenberghe et al., 1986). Figure 6.9 (left) shows the effect of some of these ions on T_C and T_N . $M/(\text{Fe} + \text{M})$ ratios suppressing the Morin transition completely (ca. <10 K) are 0.11 for Al, 0.05 for Ga, 0.04 for Cr, 0.015 for In (Sváb & Krén, 1979) and 0.038 for Ti (Curry et al., 1965). Crystallinity and the extent of Al substitution are not independent of each other, so it is difficult to separate the effect on B_{hf} due to Al substitution from that resulting from crystal-

Tab. 6.3 Exchange constants for superexchange interactions in hematite (Samuelson & Shirane, 1970; with permission)

Constant	J (K)	Fe-O-Fe bond angle
J1	6	86°
J2	1.6	94°
J3	-30	120°
J4	-23	131°

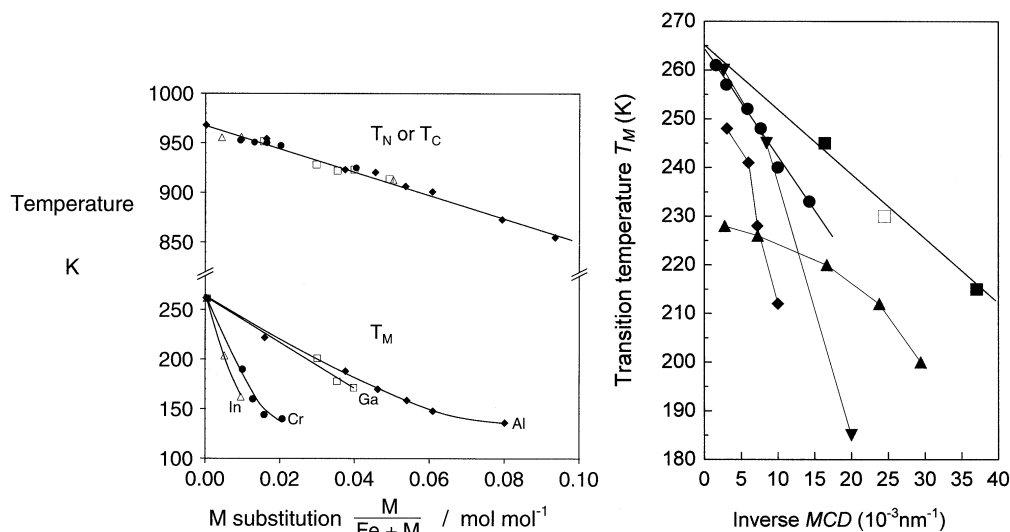


Fig. 6.9 Left: Relationship between the Curie (T_C) and Morin (T_M) temperature of hematite and the extent of structural substitution of Fe^{III} by Al, Ga, Cr and In (M) (Sváb & Krén, 1979, with permission). Right: Relationship between the Morin temperature and the inverse mean crystal dimension (MCD) for different hematites: (□) natural from Elba; (■) heating lepidocrocite

crocite above 500 °C; (▲) heating goethites at temperatures up to 900 °C; (▼) precipitation from Fe^{III} solution and heating at temperatures up to 925 °C; (◆) prepared from an oxide sol; and (○) as before but afterwards heated at 300 °C (Courtesy Dr. R.E. Vandenberghe; see also Vandenberghe et al. 2000; with permission).

lite size. Quantitative comparison between different sets of results is difficult because the crystallinity of the hematites in the different studies varied with the method of synthesis (Murad & Schwertmann; 1986; see Fig. 3.9). The Morin transition is suppressed for particles smaller than 20 nm, possibly by the increasing OH content (see above). The combination of poor crystallinity and Al substitution can lead to the coexistence of both ferro- and antiferromagnetic phases over a range of temperatures in an apparently homogeneous sample (Murad & Johnston, 1987; Vandenberghe et al. 2001). For Al-hematites with substitution of up to 0.10 mol mol⁻¹, produced from Al-lepidocrocites via maghemite (i.e. from a precursor lower in OH) by heating at 652 °C, there was a linear correlation between T_M and Al substitution of ($r^2 = 0.97$); $T_M = 238 - 641 \cdot \text{Al}/(\text{Al} + \text{Fe})$. The depression of T_M by Al was lower than with Al-hematites made from Al-goethites, which was attributed to a lower OH content (VanSan et al. 2001).

6.3.4.7 Magnetite and Maghemite

Magnetite is ferrimagnetic at room temperature and has a Curie temperature of 850 K. The two different cation sites in the structure – tetrahedral (A) occupied by Fe³⁺ and octahedral (B) occupied by Fe³⁺ and Fe²⁺ (see Chap. 2) – form the basis for two interpenetrating magnetic sublattices. Below T_C , the spins on the A and B sites

are antiparallel and, in addition, the magnitudes of the two types of spins are unequal; this causes ferrimagnetism. The spin arrangement is written as $\text{Fe}^{3+} [\text{Fe}^{3+} \text{Fe}^{2+}] \text{O}_4$. The main type of interaction is antiferromagnetic coupling via the $127^\circ \text{Fe}_\text{A}-\text{O}-\text{Fe}_\text{B}$ linkage and this is stronger than coupling on the octahedral sites. On the latter sites the electrons are thermally delocalized over the Fe^{2+} and Fe^{3+} ions and it is this delocalization that is responsible for the high conductivity of magnetite. The exchange constants are $-28, -18, 3 \text{ J(K)}$ for J_AB, J_AA and J_BB , respectively. At 118 K (the Verwey transition temperature), an ordered arrangement of Fe^{2+} and Fe^{3+} ions on the B sites exists and this inhibits electron delocalization.

The preferred direction of magnetization is along the 8 [111] cube diagonals. Al substitution lowers the hyperfine field of magnetite; there is a linear relationship between the extent of substitution and B_hf (Murad & Johnston, 1987). Particles smaller than 6 nm are super-paramagnetic at room temperature. Where the particle size and size distribution of magnetite crystals are similar, crystal morphology affects coercivity in the order: spheres < cubes < octahedra in line with the increase in the number of magnetic axes along this series of shapes. By controlling the precipitation conditions and hence particle size and morphology, magnetites with coercivities ranging from 2.4 to 20 kAm^{-1} can be produced (Meisen & Kathrein, 2000).

Maghemite is ferrimagnetic at room temperature. Measurement of T_C is difficult because maghemite transforms to hematite at temperatures above ca. 7–800 K. The Curie temperature has been estimated as lying between 820 K and 986 K (Murad, 1988).

The magnetic structure consists of two sublattices corresponding to Fe located on tetrahedral (A) sites and on the octahedral (B) sites (Néel, 1948). The atomic moments within each sublattice are parallel, but those of the two sublattices are antiparallel. Particles <10 nm in size are superparamagnetic at room temperature (Coey & Khalafalla, 1972). Magnetic coupling is influenced by the extent of aggregation: aggregation of ultrafine maghemite particles may lead to magnetic coupling between particles; i.e. ordering of the magnetic moment, which is termed superferromagnetism (Mørup et al., 1980). Jolivet and Tronc (1988) examined a suspension of 9 nm particles which had been flocculated to varying degrees and in different media. They found that the effective anisotropy constant ranged from $3.5 \cdot 10^4 \text{ Jm}^{-3}$ for compact aggregates to $1.7 \cdot 10^4 \text{ Jm}^{-3}$ for linear chains. Larger anisotropy constants (10^5 Jm^{-3}) have been reported for bigger crystallites (Coey, 1988). Sugimoto (2001) produced spindle-shaped maghemites (see chap. 14) the coercivity of which increased from 19 kAm^{-1} to 51 kAm^{-1} as the aspect ratio increased from 1 (equant particles) to 7.

Surface/interfacial effects influence the magnetic properties of ultrafine maghemite particles. Incomplete coordination of the atoms at the surface leads to a non-collinear spin configuration which reduces the magnetization of the small particles; the thickness of this canted layer has been estimated to be 1 nm (Coey, 1988). The specific saturation magnetization decreases linearly with increasing specific surface area (Mollard et al., 1977) and is also influenced by particle morphology (Batis-Landoulis & Vergnon, 1983).

Two sextets assigned to the A and B sites, can be fitted to a broadened Mössbauer spectrum. For maghemite formed via reduction of hematite to magnetite, followed

by oxidation, the effective B_{hf} s were 45.2 and 44.9 T at 275 K and 57.5 and 47.1 T at 4.2 K for the A and B sites, respectively (Da Costa et al., 1994).

6.3.4.8 Other Fe oxides

$\epsilon\text{-Fe}_2\text{O}_3$ transforms into hematite at 1040 K. It has a Curie temperature of 480 K. At room temperature, the disorderd form is antiferromagnetic with $T_N = 753$ K (Dezsi & Coey, 1973). The magnetic properties correspond to what would be expected of very small crystallites with a large (10%) number of random vacancies. Ordered $\epsilon\text{-Fe}_2\text{O}_3$ has a complex Mössbauer spectrum (Tronc et al. 1998). At 9 K it behaves as a non-collinear ferrimagnet; the hyperfine fields are canted.

$\text{Fe}(\text{OH})_2$ is difficult to investigate because it is so readily oxidized. At room temperature it is paramagnetic and is antiferromagnetic below 33 K (Miyamoto, 1976). $\text{Fe}(\text{OH})_2$ has a layer structure. In the antiferromagnetic state all spin moments within a layer are parallel and also parallel to the c -axis; spins between adjacent layers are antiparallel. There are two types of superexchange interactions; $\text{Fe}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix}\text{Fe}$ within each layer (bond angle 90°) and Fe-O-O-Fe between the layers where each Fe^{2+} ion is separated by two layers of OH^- ions.

Bernalite shows magnetic ordering of the weakly ferromagnetic type. A field of 6 T is strong enough to align the net magnetic moment so that the individual spins are close to perpendicular to the direction of the external field (McCammon et al. 1995; De Grave et al. 1999).

Wüstite is paramagnetic at room temperature and becomes antiferromagnetic at temperatures below 203–211 K; T_N depends to some extent on the concentration of defects in the structure and defects are common in this phase. Below T_N , the electron spins are ordered ferromagnetically in the (111) plane with the moments parallel to [111]; neighbouring (111) planes have opposite spins. The antiferromagnetic ordering is responsible for the slight distortion of the structure below T_N ; there is a slight elongation along one of the threefold axes parallel to the [111] direction.

6.4

Colour

6.4.1

General

The processes responsible for the colours of iron oxides are the absorption and the scattering of light. The red and yellow hues of the Fe^{III} oxides are the result of the absorption of light in the blue-green part of the visible spectrum. Where absorption is much greater than scatter over the entire visible region, iron oxides are black; the coloured pigments give rise to a mixture of scattering and absorption over this range. The green colour of bernalite is considered to arise as a result of the lack of face sharing between octahedra (see Chap. 2); there is only corner sharing and hence no absorption in the blue-green region (Birch et al., 1993).

Tab. 6.4 Some optical properties of iron oxides

Colour (Munsell)	Oxide	Refractive index	Other
Yellow-Brown 7.5YR-10YR	Goethite at 850 nm	$N_x = 2.185$ $N_y = 2.292$ $N_z = 2.304$ $N_{ave} = 2.36$	Anisotropic [§] Extreme disperison Pleochroic ^{&}
Orange 5YR-7.5YR	Lepidocrocite	$N_x = 1.94$ $N_y = 2.20$ $N_z = 2.51$	Anisotropic Weak dispersion Pleochroic
Bright red R-2.5YR	Hematite at 689 nm	$N_o = 2.98$ $N_e = 2.75$ $N_{ave} = 2.87$	Strongly birefringent [§] Strong dispersion
Black	Magnetite	2.42	Isotropic
Black	Wüstite	2.32	Isotropic

§ Most minerals polarise light that passes through them, i.e. show anisotropic behaviour

\$ Birefringence—the maximum difference between the refractive indices of a mineral

& Pleochroism—exhibits two different colours upon rotation of the stage of the polarising microscope

The iron oxide colours can be characterized by their spectral reflectance curves or the Kubelka-Munk remission function (Chap. 7). The most important optical properties of the iron oxides as pigments are the light scattering and (above all) the absorption coefficients. These in turn determine pigment properties such as hiding power and tinting strength which are important in both the paint industry and in the geosciences. Both coefficients depend on the particle size and the refractive index. The latter depends on the wavelength of the light and, in the case of anisotropic iron oxides, on the illuminant and the viewing direction; the acicular iron oxides have three different refractive indices at each wavelength (Tab. 6.4). The scattering and absorption coefficients of goethite and hematite vary with wavelength and also from one sample to another, most probably owing to variations in crystal size and morphology (see Fig. 6.13, below) (Barrón & Torrent, 1986). Information about the optical properties of the iron oxides is obtained with the polarising microscope (see Shelly, 1975)

As a pigment, each iron oxide has an optimum particle size which is that with the maximum scattering cross section. This optimum particle size is lower, the higher the refractive index of the mineral. For hematite, the size corresponding to the maximum in scattering/absorption cross section is ca. 1 μm . As the particle size decreases, the relative scattering cross section drops to zero and the relative absorption cross section levels out. As a result, very small particles of hematite are transparent.

There is a variety of systems used to quantify colour and to assist in the comparison of colours, two important ones being the CIE-Lab system and the Munsell colour classification. Details of these systems are given in Wyszecki & Styles (1982) and Heine & Volz (1993). Very briefly, the CIE systems are based on the principle of tri-

chromaticity because the human eye responds to only three colour components corresponding to the tristimulus values X, Y and Z. The tristimulus values can be computed from reflectance spectra and can be mathematically converted to coordinates to create a uniform colour space. In the CIE-LAB system these cartesian coordinates are L^* (lightness or value), a^* (redness-greenness) and b^* (yellowness-blueness). Different colours can be expressed in terms of L^* , a^* and b^* .

Instruments for quick measurement of L^* , a^* , and b^* , even in the field are available. The colour saturation is given by $\sqrt{a^{*2} + b^{*2}}$ and the hue by the arctan (b^*/a^*). Figure 6.10 (left) demonstrates that synthetic goethites, lepidocrocites and hematites can be differentiated in the a^* - b^* colour space. It is obvious that hematites are separated from goethites by their significantly higher redness (a^*) and lower yellowness (b^*), but this is also true for lepidocrocites, although to a lesser extent. The colour change during the conversion at 95 °C of 2-line ferrihydrite to goethite at pH 12.2 and to hematite at pH 7.5 (Fig. 6.10 right) can also be followed in this way: the goethite develops its yellow colour essentially parallel to the b^* -axis, whereas with hematite, the colour moves more in both in the yellow and the red directions. At intermediate pHs the colours were intermediate between red and yellow (Nagano et al., 1994). An example of the use of b^* to quantify the amount of Fe oxides in soils is given in Chapter 16.

In soil and other geosciences, colour is commonly measured using the Munsell colour classification system. This system defines colour in terms of hue H (position of colour in the spectrum), chroma C (the purity of the hue going from the grey to the pure colour) and value V (the lightness of the colour on a scale ranging from black to white). The reflectance measurements can be converted into the characteristic parameters or coordinates of the different measurement systems.

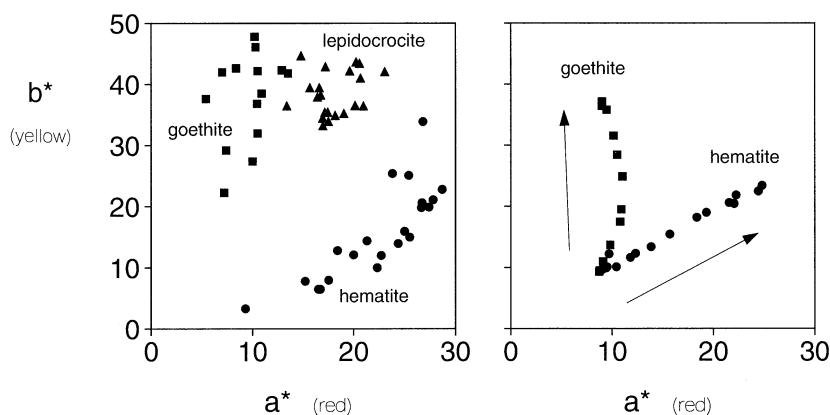


Fig. 6.10 Left: Placement of various synthetic goethites (G), lepidocrocites (L) and hematites (H) in CIE $L^*a^*b^*$ colour space. Right: Development of a^* and b^* in the CIE $L^*a^*b^*$ colour space during the transformation of ferrihydrite (common starting point) to goethite or hematite, respectively (Nagano et al., 1994, with permission).

6.4.2

Colours

Iron oxides are responsible for the vivid colours of many rocks and soils. The typical yellow-red to purple red colours of the so-called red beds are due to hematite (Torrent & Schwertmann, 1987). The strong influence of hematite on soil colour is referred to in various languages and appears in the terms red earths, terra rossa and krasnozems (see Chap. 15 & 16).

To the naked eye, goethite and akaganéite appear yellow-brown, lepidocrocite orange and hematite usually red (Plate 6.I). Feroxyhyte and ferrihydrite are dark reddish brown, maghemite brown to brownish red and magnetite and wüstite are black. Table 6.5 gives the colour range of eight of the iron oxides in the two most common colour systems, Munsell and CIE L^*a^*b (see Fig. 6.10, left). This table was compiled from chromametre measurements on 165 synthetic samples (Scheinost & Schwertmann, 1999). It shows that hematite has the most reddish average hue, while feroxyhyte, ferrihydrite, akaganéite, lepidocrocite, maghemite, schwertmannite and goethite exhibit increasingly yellower hues. The redder hues of hematite and, to a lesser extent, of feroxyhyte are due to face sharing octahedra between which the Fe-Fe distance is only 0.29 nm. This strongly enhances electron pair transitions. In contrast, the other minerals contain only edge and corner sharing octahedra and the Fe-Fe centres are 0.30–0.33 and 0.35 nm apart, respectively (see chap. 2) and this leads to yellower hues. Magnetite and partly oxidized magnetite are black or almost black

Tab. 6.5 Munsell hue, value and chroma and CIE $L^*C^*H^\circ$ colours of synthetic Fe oxides (mean, minimum – maximum). N = number of samples (Scheinost & Schwertmann, 1999; with permission)

	N	Hue	Value	Chroma	L^*	C^*	H°
Akaganéite	8	5.4 YR	3.9	5.8	40	35	63
		4.4 YR–8.0 YR	2.8–5.0	4.4–6.9	29–51	25–43	55–71
Ferrihydrite	10	4.4 YR	3.8	4.7	39	27	57
		2.8 YR–5.5 YR	2.3–5.4	1.9–6.6	23–56	10–39	44–63
Feroxyhyte	11	3.9 YR	3.8	5.9	39	34	56
		1.5 YR–5.4 YR	3.4–4.7	4.2–7.0	35–48	24–41	45–63
Goethite	54	0.5 Y	6.1	7.1	63	47	80
		8.1 YR–1.6 Y	4.9–6.9	6.2–9.6	51–71	41–62	72–84
Hematite	44	0.3 YR	3.6	3.6	37	29	42
		3.5 R–4.1 YR	2.4–4.4	2.4–4.4	25–45	9–42	21–57
Lepidocrocite	26	6.7 YR	5.5	8.3	57	50	68
		4.9 YR–7.4 YR	4.6–5.9	7.3–9.9	47–61	45–60	63–70
Maghemite	7	8.3 YR	3.1	3.2	32	20	68
		6.2 YR–9.4 YR	2.5–3.6	2.5–4.1	25–37	15–24	61–72
Schwertmannite	5	8.8 YR	6.2	7.9	64	50	75
		7.7 YR–9.2 YR	5.6–6.5	7.3–9.1	58–66	45–58	71–77

because the structure contains both Fe^{II} and Fe^{III} which causes intervalence charge transfer (IVCT).

Goethite, hematite, lepidocrocite and ferrihydrite can be distinguished on the basis of hue and chroma (Fig. 6.11): hematite is always redder than 4.1 YR and goethite is yellower than 8.1 YR. Ferrihydrite and lepidocrocite have intermediate hues and are separated by chroma. The colour of maghemite is unique owing to values lower than 3.6 and hues yellower than 6.2 YR. Feroxyhyte overlaps hematite in hue and value, but has a higher chroma. Only akaganéites with a hue yellower than 5.5 YR can be reliably distinguished from ferrihydrite. Schwertmannite can be distinguished from goethite only if it is redder than 8.1 YR.

Depending on the type of mineral, individual samples may deviate from the average by 3.8 units of hue (hematite), 1.6 units of value (ferrihydrite) and 2.8 units of chroma (ferrihydrite). Variations in crystallinity, particle shape and size, aggregation and also cation substitution, cause variations in the colour of a particular mineral. Differences in *crystallinity* cause a broader distribution of electron transition bands and hence a smoother absorption spectra with a less vibrant appearance. Massive crystals or dense aggregates of goethite and hematite are strongly absorbing and so appear dark brown or black. Their specific colour only appears when powdered and the so-called streak test – pushing the mineral over a rough ceramic surface – brings out this colour. This is also illustrated with an example from a workshop producing hematite jewellery from large black hematite crystals (specularite); the hands of the person shaping the massive crystals are stained red from the hematite powder.

Particle shape also influences the orientation of particles towards the incident light. For instance, platy particles may absorb along one crystallographic axis, while spherical particles may absorb along randomly oriented axes. As the absorption spectrum varies with the crystallographic orientation, this may have a marked effect on colour. Acicular hematite, for example has a higher reflectance and hence higher scattering power in the long wavelength region of the spectrum than a more symmetrical particle and, therefore, has a yellower hue, higher purity and higher radiance factor

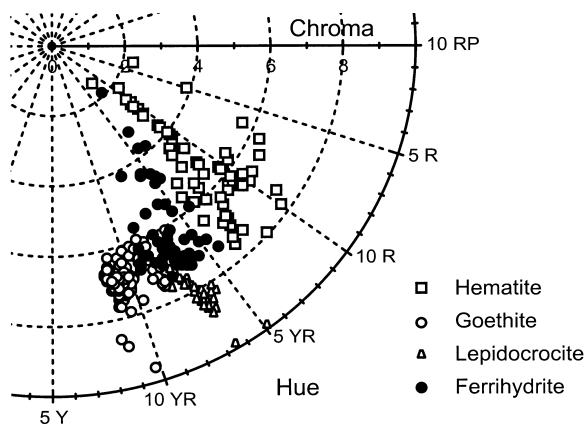


Fig. 6.11 Munsell colours of synthetic hematite, ferrihydrite, lepidocrocite, and goethite samples (Courtesy A.C.Scheinost; Scheffer & Schachtschabel, 2002, *Lehrbuch der Bodenkunde*, S. 269, Spektrum Akademischer Verlag, Heidelberg, Berlin. 15. Aufl.; with permission; Schwertmann & Cornell, 2000, with permission)

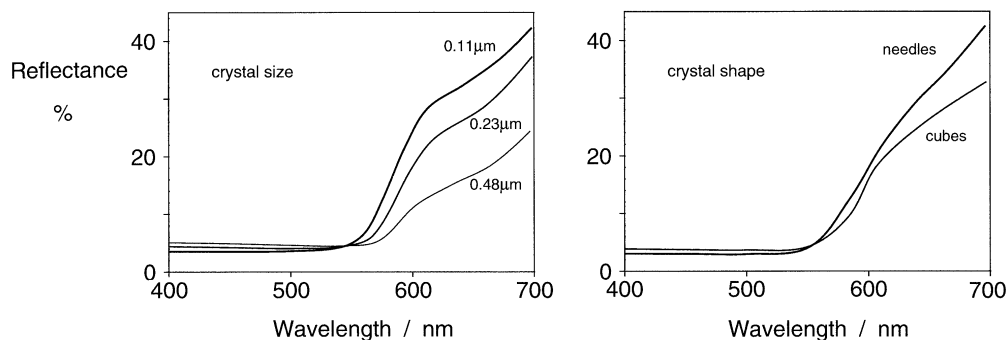


Fig. 6.12 Diffuse reflectance spectra of hematites of different crystal size (left) and different crystal shape (right) (Hund, 1981, with permission).

(Fig. 6.12, right) (Hund, 1981). As the aspect ratio of the goethite crystals increases (i.e. long, very thin needles) the sample develops a greenish tinge.

The colour variation of powders with *particle size* can be seen in Plate 6.11 (Schwertmann, 1993). Goethite and akaganéite crystals of 0.3–1 μm are yellow and become darker as the particle size decreases: As the needle length of goethite falls from 0.8 to 0.05 μm , the colour shifts towards darker values and more yellow hues (Scheinost et al. 1999). In a similar manner, the colour of lepidocrocite changes from the bright orange of the larger crystals to the dark brownish-orange of the smaller crystals. As the particle diameter of hematite increases from 0.1–1.0 μm , the hue changes from yellow-red to blue-red (Schwertmann, 1993). For crystals >5 μm , the blue component of the spectrum increases sufficiently for the crystals to appear purple. Kerker et al. (1979) noted that suspensions of hematite with particle sizes <0.1 μm were orange, those 0.1–0.5 μm red and those > 1.5 μm purple. Correspondingly, spectra of hematite show an increase in reflectance in the red range as the particle size decreases from 0.48 to 0.11 μm (Fig. 6.12 left). Hematite pigment particles of ca. 10 nm in size are transparent when dispersed in paint binder (Gaedcke, 1993).

Red hematite can be converted to purple hematite by increasing the size sufficiently, for example, by heating to >800 $^{\circ}\text{C}$ (von Steinwehr, 1969). There is some evidence that associations of small, platy, hematite crystals into orientated aggregates (e.g. in red beds) also cause a colour shift towards purple (Torrent & Schwertmann, 1987).

Replacement of some Fe atoms in the crystal by other metals can also modify the colour. The transition metals add their own electron transition bands to those of iron thus causing a red shift with increasing amounts of Cr, Co and Ni and a green shift with increasing V and Mn (Fig. 6.13). Mn substituted goethite, therefore, appears olive-brown to blackish (Stiers & Schwertmann, 1985), Cr-goethite brownish (Schwertmann et al., 1989) and V-goethite greenish. The dominant wave length (Bedidi et al. 1992) of V-goethites decreased from 578 to 548 nm while the total reflection intensity decreased from 36 to 15% as $\text{V}/(\text{Fe} + \text{V})$ increased from zero to 0.06

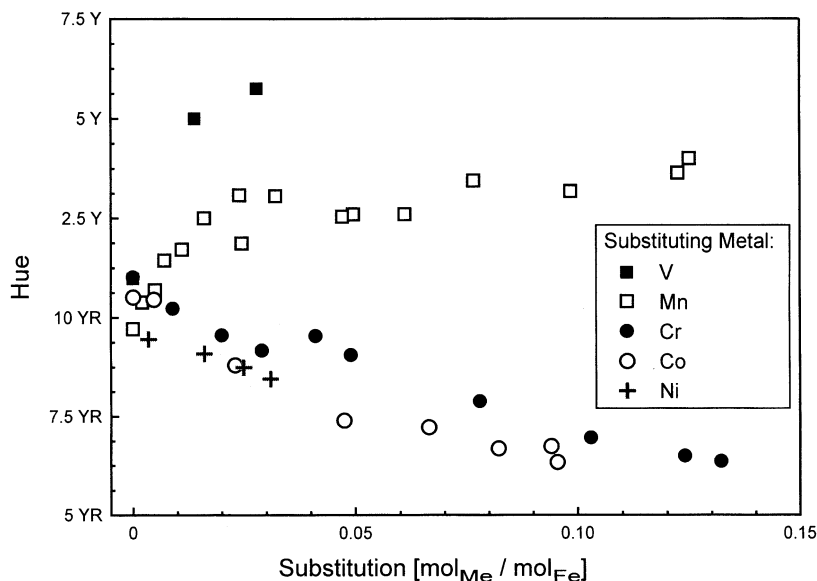


Fig. 6.13 Munsell hue of goethite as a function of substitution with transition metals (Courtesy A.C.Scheinost; Schwertmann & Cornell, 2000, with permission)

(Schwertmann & Pfab, 1994) (see Plate 6.II). Mn substituted hematites are blackish. In case of Al substitution, the observed shift towards redder hues is due mainly to the associated decrease in particle size (Scheinost et al. 1999). Structural Al does not significantly influence the hue and chroma of synthetic Al-hematite, although the crystals become lighter (Munsell value increases) (Barrón & Torrent, 1984; Kosmas et al., 1986).

6.4.3

Pigment properties

Two important properties of pigment iron oxides are tinting strength and hiding power. Tinting strength is a measure of the capacity of the pigment on the basis of its absorption constant, to impart colour to other light scattering substances. All iron oxides have high tinting strengths. The tinting strength of a powder increases as both the particle size decreases and the particle size distribution widens. For example, the tinting strength of magnetite has been observed to rise even though the average particle size remained constant; this was because the particle size distribution continued to decrease (Hund, 1981). Coatings too thin to be detected by XRD nevertheless strongly colour soils (see Plate 16.I) and sediments. The tinting or pigmenting power of hematite is far greater than that of goethite; a few percent of hematite in a mixture with goethite can mask the yellow goethite colour. Barrón and Torrent (1986) developed redness indices based on the Munsell colour notation H, C, V, and

the CIE colour system. They reflect the hematite content perfectly in mixtures of synthetic hematite and deferrated (grey) soils with up to 15% hematite (saturation above that), but less accurately in hematitic soils. Goethite does not interfere. Hematite has a greater hiding power than goethite – $30\text{--}60\text{ m}^2\text{ kg}^{-1}$ and $15\text{--}20\text{ m}^2\text{ kg}^{-1}$, respectively (Fuller, 1974). Another pigment property is the oil absorption in the paint – 32–52 for FeOOH and 13–76 for hematite. The exact value depends on the method of production.

7

Characterization

7.1

Introduction

This chapter reviews the various methods used to identify and characterize iron oxides. Most of these are non-destructive, i.e. the oxide remains unaltered while being examined. These methods involve spectroscopy, diffractometry, magnetometry and microscopy. Other methods, such as dissolution and thermal analysis destroy the sample being examined. Only the principle of each method is given here. The main weight is put on the information about Fe oxides which can be extracted from the analytical results obtained by the different techniques together with references to relevant studies. A detailed description of each technique can be found in the appropriate texts listed in each section.

Spectroscopy produces spectra which arise as a result of interaction of electromagnetic radiation with matter. The type of interaction (electronic or nuclear transition, molecular vibration or electron loss) depends upon the wavelength of the radiation (Tab. 7.1). The most widely applied techniques are infrared (IR), Mössbauer, ultraviolet-visible (UV-Vis), and in recent years, various forms of X-ray absorption fine structure (XAFS) spectroscopy which probe the local structure of the elements. Less widely used techniques are Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), secondary ion imaging mass spectroscopy (SIMS), Auger electron spectroscopy (AES), electron spin resonance (ESR) and nuclear magnetic resonance (NMR) spectroscopy.

Diffractometry involves interaction of X-rays (X-ray diffraction, XRD), electrons (electron diffraction, ED) or neutrons (neutron diffraction, ND) with the atoms of a solid. Of these methods, X-ray diffraction is by far the most widely used. In contrast to spectroscopic and other methods, XRD recognizes the regular, long-range arrangement of atoms in a crystal by which a mineral (together with its chemistry) is defined, and, thus, is the most reliable tool for identification of a particular iron oxide. *Thermal analysis* registers the heat released or consumed (differential thermal analysis, DTA), the weight loss (thermal gravimetric analysis, TGA), or the energy input (differential scanning calorimetry; DSC), compared to that for an inert standard, upon application of heat. A fourth group of methods, especially useful for characterizing Fe oxides, and summarized as *magnetometry*, investigates the bulk magnetic properties arising from the special spin structure of the iron atom (see chap. 6).

Tab. 7.1 The electromagnetic spectrum

<i>Spectral region</i>	<i>Approximate wavelength range</i>	<i>Energy transitions induced</i>
Radiofrequency	30 cm–3 km	Molecular rotations
Microwave	0.1–30 cm	Molecular rotations
		Electron spin resonance
Far infrared	50–1000 μm	Molecular rotations
Infrared	2.5–50 μm	Molecular vibrations
Near infrared	0.8–2.5 μm	Excitation of valence electrons
Visible	400–799 μm	Excitation of valence electrons
Ultraviolet	200–400 μm	Excitation of valence electrons
Vacuum ultraviolet	10–200 nm	Ionization by removal of outer electrons
X-rays	0.006–100 nm	Ionization by removal of core electrons
Gamma	0.001–0.1 nm	Nuclear transitions

In addition to all these methods, optical and *electron microscopy* (EM) are extensively used to examine iron oxides. EM includes transmission (TEM) and scanning (SEM) electron microscopy, and the two surface probing techniques, viz. scanning tunnelling (STM) and scanning or atomic force microscopy (SFM/AFM) (Hochella, 1990, 1995). High-Resolution TEM (HRTEM) achieves a point-to-point resolution of up to 0.2 nm (Janney et al. 2000) and produces crystal lattice images. These microscopic techniques can be combined with energy-dispersive spectrometry, such as electron energy loss spectroscopy (EELS) for chemical analysis. They provide information about the structure, microtopology and reactivity of the surface, the electronic characteristics and extent of metal substitution and, in many cases, have been used to monitor chemical reactions and interactions. A number of the above techniques including XPS, SIMS, AES, electron microscopy and electron diffraction are carried out under vacuum and these conditions may alter the Fe oxide surface to some extent. Under ultra high vacuum (UHV) conditions, crystal surfaces may undergo either relaxation or reconstruction, i.e. the surface atoms adopt new positions. These processes may also occur as a result of cleavage of crystals, ion bombardment or high temperature annealing under UHV. *Relaxation* involves a shift from the interatomic distances found in the bulk material and a change in bond angles: it occurs in the first and second atomic layers. *Reconstruction* involves changes in bond length and angles and also in the number of nearest neighbours of atoms. 1×1 surfaces are unchanged, whereas in a 2×1 reconstructed surface, one edge of the surface unit cell has doubled, but the other is unchanged.

7.2

Infrared spectroscopy

Infrared spectra arise as a result of interactions of iron oxides with electromagnetic radiation (photons) in the wavelength range 1–300 μm (i.e. wave numbers of 10,000–33 cm^{-1}). These interactions involve excitation of vibrations or rotation of molecules in their ground electronic state and are associated with stretching deformations of the interatomic bonds and bending deformations of the interbond angles. The frequency of radiation absorbed depends upon the rotational energy levels and the force constants of the interatomic bonds (Farmer, 1974).

An infrared spectrum is a plot of percent radiation absorbed versus the frequency of the incident radiation given in wavenumbers (cm^{-1}) or in wave length (μm). A variation of this method, diffuse reflectance spectroscopy, is used for samples with poor transmittance, e.g. cubic hematite crystals. Increased resolution and sensitivity as well as more rapid collection of data is provided by Fourier-transform-IR (FTIR), which averages a large number of spectra. Another IR technique makes use of attenuated total reflectance FTIR (ATR-FTIR) often using a cylindrical internal reflectance cell (CIR) (e.g. Tejedor-Tejedor & Anderson, 1986). ATR enables wet systems and adsorbing species to be studied *in situ*.

For iron oxides, IR spectroscopy is useful as a means of identification. Hematite crystals in films that were too thin (<70nm) to be characterized by XRD were shown by IR to be oriented with the c-axis perpendicular to the surface of the film (Yubero et al. 2000). This technique also provides information about crystal morphology, degree of crystallinity and the extent of metal (especially Al) substitution because these properties can induce shifts in some of the IR absorption bands. It is also widely used both to obtain information about the vibrational state of adsorbed molecules¹⁾ (particularly anions) and hence the nature of surface complexes (see Chap. 11) and to investigate the nature of surface hydroxyl groups and adsorbed water (see Chap. 10). Typical IR spectra of the various iron oxides are depicted in Figure 7.1. Impurities arising either from the method of preparation or from adsorption of atmospheric compounds can produce distinct bands in the spectra of these oxides – namely at 1700 cm^{-1} (oxalate), 1400 cm^{-1} (nitrate) and 1300 and 1500 cm^{-1} (carbonate).

7.2.1

Goethite

The absorption bands of goethite arise, as do those of the other FeOOH polymorphs, from Fe-OH and Fe-O vibrations. There are 36 possible Fe-O vibrations and 12 hydroxyl vibrations. Of these, 12 Fe-O and 5 hydroxyl vibrations (all B type) are infrared active, although not all of these are observed experimentally (Table 7.2). The same bands are detected whether the sample is examined by transmission, diffuse reflec-

1) A comprehensive list of the vibration modes for a range of oxyanions is given in table 1 of Suarez et al. 1999.

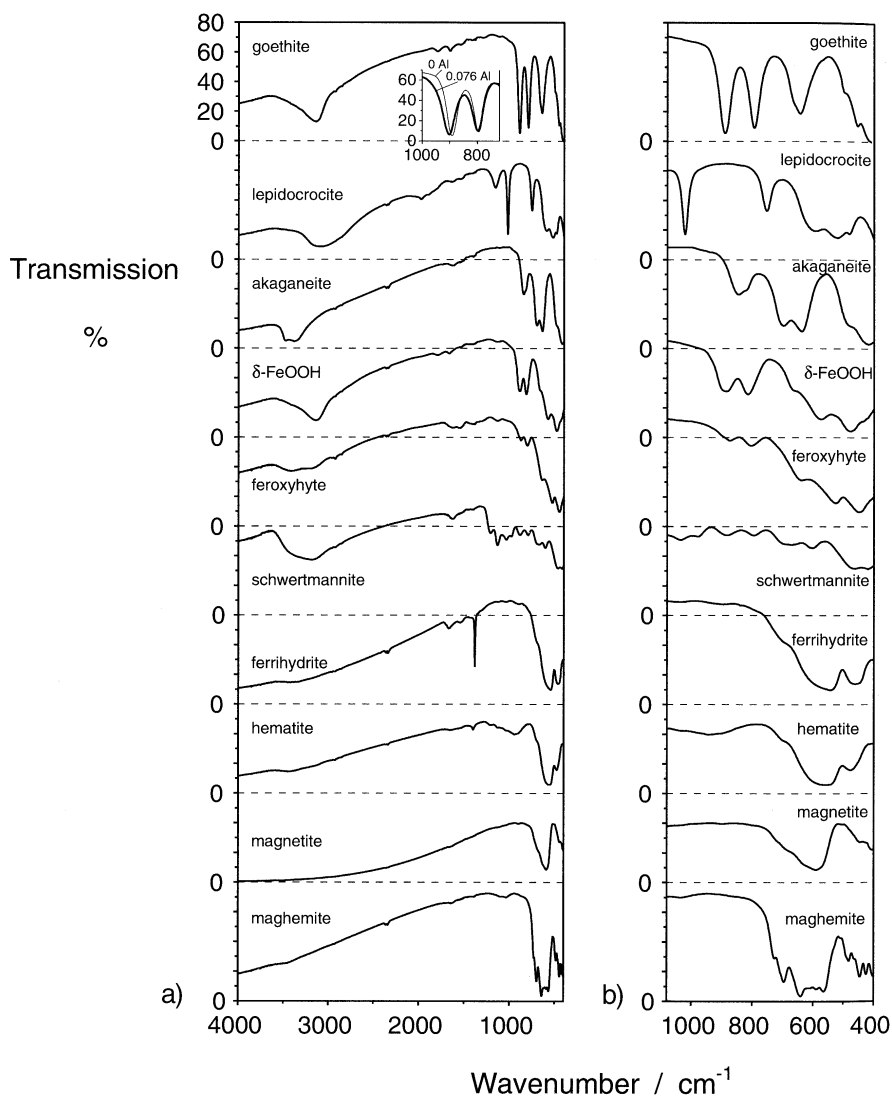


Fig. 7.1 Infrared spectra of iron oxides in the range 400 to 4000 cm^{-1} (ca. 1 mg in 300 mg KBr). a) Wave number range 1000–4000 cm^{-1} ; b) wave number range 400–1000 cm^{-1} . The insert in the goethite spectrum shows that the two OH bending vibrations shift to higher wave

numbers as Al (here $\text{Al}/(\text{Fe} + \text{Al}) = 0.076 \text{ mol mol}^{-1}$) enters the structure with the band at 900 cm^{-1} shifting more than that at 800 cm^{-1} . The sharp peak in the ferrihydrite spectrum is due to NO_3^- . The arrow indicates the band at 3400 cm^{-1} for hematite.

Tab. 7.2 Infrared bands of goethite (Cambier, 1986) and lepidocrocite (Lewis & Farmer, 1986) (with permission)

Vibration	Specific symmetry	Wave numbers of bands/cm ⁻¹		
		Lepidocrocite		Goethite
		Rods	Plates	
Surface OH v stretch	B _{2u}	3620, 3525	3160	3660, 3484 3140
		3060		
	B _{3u}		2850	
δ _{OH} in plane bend	B _{2u}	1150	1160	892
	B _{3u}	1018	1018	
γ _{OH} out of plane bend	B _{1u}	752	742	795
τ _O	B _{3u}	610	510	630 [§]
	B _{2u}	510	540	~495 ^{sh}
	B _{1u}	478	480	449
τ _{OH}	B _{2u}	357	355	397 ^{§§}
	B _{1u}	270	270	
	B _{3u}	223	220	263

§ Fe-O symm. stretch parallel to *a*; §§ Fe-O antisymm. stretch parallel to *c*; sh shoulder

tance or internal reflectance spectroscopy, but their intensities and relative intensities may vary (Parfitt et al., 1976; Rochester & Topham, 1979; Tejedor-Tejedor & Anderson, 1986). The intensities of the OH deformation bands as obtained by transmission IR are the reverse of those obtained by ATR. The correct assignment of many of the spectral bands was first made by Schwarzmunn and Sparr (1969) using deuterium exchange. Subsequently Verdonck et al. (1982) carried out a normal coordinate analysis of the spectrum of goethite.

An intense band due to the bulk hydroxyl stretch is observed at 3140 cm⁻¹. Two far less intense bands at 3660 and 3484 cm⁻¹ can be attributed to the surface hydroxyl groups. In general, these bands can only be detected on an evacuated surface. The most reasonable assignment for these bands appears to be that of Russell et al. (1974) who found that the band at 3660 cm⁻¹ disappeared completely when the surface was phosphated and so attributed it to the singly coordinated OH groups; the band at 3484 cm⁻¹ was not replaceable by adsorbed phosphate and was considered to consist of contributions from the doubly and triply coordinated OH groups.

The OH bending bands at ca. 892 cm⁻¹ (δ-OH) and 795 cm⁻¹ (γ-OH) which vibrate in and out, respectively, of the (001) plane are important diagnostic bands and also provide information about crystallinity and the extent of Al-substitution. The frequencies of these vibrations depend on both the OH site and on resonance phenomena (Cambier, 1986). Decreasing crystallinity causes the bands to broaden, the frequency of the OH bending bands to decrease and that of the OH stretch to increase. These shifts in band position are due to a decrease in the strength of hydrogen bonding in the unit cell. The OH bending bands also move closer together, with the separation decreasing from 97 cm⁻¹ for well crystallized to 94 cm⁻¹ for poorly

crystallized goethite (Schwertmann et al., 1985; Cambier, 1986). As the level of Al-substitution increases from zero to its maximum of $0.33 \text{ mol mol}^{-1}$, the separation of the bending bands increases from 97 cm^{-1} to 140 cm^{-1} (see insert in Fig. 7.1) (Schulze & Schwertmann, 1984, 1987). This effect becomes weaker as the sample crystallinity decreases. In fact, as Al substitution is often associated with small particle size/poor crystallinity, particularly for soil goethites, it is often difficult to separate the effect of substitution from that of crystallinity. Structural incorporation of up to $0.095 \text{ mol mol}^{-1}$ Co shifted the γ -OH and δ -OH bands from 793 to 796 and from 893 to 906 cm^{-1} , respectively (Gasser et al. 1996).

Particle morphology and crystallinity influence the position of the symmetric Fe-O stretch at ca. 630 cm^{-1} because this vibration, which corresponds to a transverse moment, lies in the (010) plane; as the crystallinity of the sample falls and the unit cell a length increases (see Chap. 2), the frequency of this band decreases (Cambier, 1986a). The band at 397 cm^{-1} which corresponds to an antisymmetric Fe-O vibration parallel to (100) is insensitive to particle shape and crystallinity.

7.2.2

Lepidocrocite

The IR bands and their assignments are shown in Table 7.2. The surface hydroxyl groups give rise to weak bands at 3620 and 3525 cm^{-1} ; it has been suggested that the band at 3620 cm^{-1} corresponds to doubly coordinated OH groups on the (001) plane (Lewis & Farmer, 1986). The bulk OH stretch lies between 2850 and 3160 cm^{-1} depending on particle morphology. The stretch vibrations can vary between the upper longitudinal frequency and the lower transverse frequency according to crystal morphology. As the crystals change from plates to rods the vibrations in the [100] direction decrease in frequency, whereas those parallel to the [100] direction are unaffected (Tab. 7.2). The in (010) plane bending band lies at 1018 cm^{-1} and the out-of-plane bend vibration at ca. 750 cm^{-1} . Aluminium substitution shifted the position of the OH-stretch from 3130 to 3200 cm^{-1} and the out-of-plane OH-bend from 750 to 733 cm^{-1} (Schwertmann & Wolska, 1990). This behaviour has been interpreted as arising from a weakening of the hydrogen bonding between the zig-zag sheets of $\text{Fe}(\text{O},\text{OH})_6$ octahedra due to a decrease in sample crystallinity.

7.2.3

Ferrihydrite

The IR bands are at 3615 cm^{-1} (free surface OH groups), 3430 cm^{-1} (bulk OH stretch) and at 650 cm^{-1} and 450 cm^{-1} (bulk OH deformations). Russell (1979) found that most OH groups were readily accessible to deuterium exchange which suggested that there is little distinction between the surface and the bulk OH groups. The large half width of the band at 3615 cm^{-1} (60 cm^{-1}) is evidence for a disordered crystal structure; this band is broader in 2-line than in 6-line ferrihydrite. Ferrihydrite containing a few percent Si shows a broad, intense band at 940 cm^{-1} (Schwertmann & Thalmann, 1976; Carlson & Schwertmann, 1981; Parfitt et al., 1992; Hansen et al.,

1994). This band is at a lower frequency than that of the Si-O stretch in pure Si oxide gel (1080 cm^{-1}) probably because the Si-O stretch is influenced by neighbouring Fe atoms. For adsorbed arsenate and selenate on ferrihydrite, Harrison & Berkheiser (1982) reported a poorly resolved doublet at 805 and 875 cm^{-1} , and weak bands at 700 cm^{-1} and at 820 , 880 and 910 cm^{-1} respectively. These were attributed to splitting of the fundamental ν vibration.

7.2.4

Hematite

Hematite has six infrared active modes in two of which the dipole moments are parallel, and in the others, perpendicular to the c -axis (Tab. 7.3). As a result of this, the positions of the bands are sensitive to particle size and shape (Rendon & Serna, 1981). Increasing Al substitution from 0 to $0.125\text{ mol mol}^{-1}$ shifted the IR bands from 574 to 530 cm^{-1} , 478 to 456 cm^{-1} and 352 to 314 cm^{-1} (Kosmas et al., 1986); the band at 620 cm^{-1} moved to 650 cm^{-1} as the Al substitution increased from 0 to 0.15 mol mol^{-1} (Stanjek, 1991). The surfaces of the crystals are covered with hydroxyl groups (see Chap. 10) the vibrations of which appear in the IR spectrum. Rochester and Topham (1979a) claim to have detected 11 such bands the most important of which are at 3720 (shoulder), 3700 , 3635 , 3490 (shoulder), 3435 (shoulder) and 3380 cm^{-1} . They are all OH stretch vibrations. Strictly speaking, hematite contains no structural OH groups. However, the intensity of the 3400 cm^{-1} band of a hematite formed in an aqueous system decreased upon heating at from 200 up to 800°C due to reduction of structural OH from ca. 0.5 to $<0.1\text{ mol mol}^{-1}$ ($n = 16$; $r = 0.67$) (Stanjek and Schwertmann (1992).

Tab. 7.3 Infrared bands of hematite (Rendon & Serna, 1981; with permission)

Specific	Symmetry	Wave numbers of bands/ cm^{-1}		
		Calculated	Observed	
			Laths	Spheres
A_{2u}	ω_l	662	645	—
	ω_t	526		
E_u	ω_l	662	525	548
	ω_t	524	525	548
E_u	ω_l	494		471
	ω_t	437	440	
A_{2u}	ω_l	414	400	397
	ω_t	299		
E_u	ω_l	368		337
	ω_t	286	300	
E_u	ω_l	230	230	
	ω_t	227		

The longitudinal vibrations (A_u) are parallel and the transverse vibrations (E_u) perpendicular to the c -direction.

7.2.5

Other iron oxides

A recent FTIR spectrum of a synthetic *akaganéite* obtained by transmittance ATR showed bands at $3480 + 3390$ (doublet) (OH- and H_2O stretch), 1630 (OH-bending), $850 + 820$ (doublet) (?), 650 , 490 , and $\sim 420\text{ cm}^{-1}$ (Fe-O stretch). Additional bands (1096 , 1050 , 698 cm^{-1}) were found only for samples in KBr or CsI discs and were, thus, considered to be artefacts (Murad and Bishop, 2000). Very weak bands at 3659 , 3686 and 3723 cm^{-1} have been attributed to surface OH groups (Ishikawa et al., 1986). The IR spectrum of *schwertmannite*, which has a structure akin to that of *akaganéite*, has an Fe-O stretch at ca. 700 and $410\text{--}490\text{ cm}^{-1}$, an OH stretch at 3370 cm^{-1} , absorption bands due to $\nu_1(\text{SO}_4)$ at 970 cm^{-1} , $\nu_4(\text{SO}_4)$ at 610 cm^{-1} , and a splitting of the ν_3 fundamental of SO_4 at $1170\text{--}1212$, $1110\text{--}1140$, and $1040\text{--}1070\text{ cm}^{-1}$ (Bigham et al., 1990; Schwertmann et al., 1995; Carlson et al. 2002). The sulphate bands are attributed to both sulphate in the tunnels and to adsorbed surface sulphate; their intensity varies from sample to sample.

The IR spectrum for $\delta\text{-FeOOH}$ shows an OH stretch at 3130 cm^{-1} , OH bending bands at 1124 , 890 and 810 cm^{-1} and Fe-O stretch bands at 580 and 480 cm^{-1} (Okamoto, 1968). In its poorly crystalline form as *feroxyhyte*, $\delta\text{-FeOOH}$, this material shows similar, but less well expressed features. *High pressure FeOOH* shows a broad band at 2800 cm^{-1} due to the bulk OH stretch, a doublet at 1150 and bands at 970 and 685 cm^{-1} corresponding to OH bending vibrations and an Fe-O stretch, respectively (Pernet et al., 1973).

The infrared bands for the surface OH groups of *maghemite* are found at 3740 and 3725 cm^{-1} (both attributable to singly coordinated OH), 3675 (strong) and 3640 cm^{-1} (Busca et al., 1993). In the Fe-O range, fine-grained, synthetic maghemite shows broad IR bands at 700 , $640\text{--}660$, 620 , 580 , 560 , 460 , 430 , 390 and 305 cm^{-1} (Poling, 1969; Taylor & Schwertmann, 1974). The spectrum of *magnetite* has broad bands at 580 and 400 cm^{-1} (Poling, 1969; Keiser et al., 1982). The IR spectrum of *wüstite* shows one, very broad band at 490 cm^{-1} with another, weak, broad band in the range $400\text{--}250\text{ cm}^{-1}$ (Tarte et al., 1969; Raman et al., 1991). For $\text{Fe}(\text{OH})_2$ a sharp band at ca. 3600 cm^{-1} (OH-stretching) and a broad one at 480 cm^{-1} (OH translational mode) was found; *green rust I* showed bands at 3540 , 800 and 670 cm^{-1} (Misawa et al., 1969).

7.3

Raman spectroscopy

Raman spectra are the result of scattering of electromagnetic radiation by the molecules of the solid (Griffith, 1974). These spectra provide complementary information to that from infrared spectra. They are, however, not measured in the infrared region, but in either the ultraviolet or visible regions depending on the source of radiation. Active Raman vibrations are those that produce a change in the polarization of the system. The bands for goethite, lepidocrocite, hematite, magnetite and maghemite are listed in Table 7.4 (see also de Faria et al. 1997). The positions of the bands

Tab. 7.4 Raman wave numbers (Oh et al. 1998; with permission); Bold and underlined refer to the strongest and next strongest band; [§] (from Mazetti & Thistlethwaite; 2002; with permission)

Goethite	205; 247; <u>300</u> ; 386 ; 418; 481; 549
Lepidocrocite	219; 252 ; 311; 349; <u>379</u> ; 528; 638;
Akaganeite	<u>314</u> ; 380; 549 ; 722
Schwertmannit [§]	294; 318; 350; 421 ; <u>544</u> /580 ^{sh} ; 715; 981;
δ-FeOOH	297; 392 ; <u>666</u> ;
Ferrihydrite; 6-line [§]	<u>370</u> ; 510; 710 ;
Hematite	<u>226</u> ; 245; 292 ; 411; 497; 612;
Magnetite	532; 667 ;
Maghemite	<u>381</u> ; 486; 670 ; <u>718</u>
Green rust	420; 510

sh shoulder

for magnetite and maghemite are sufficiently different for these compounds to be distinguished between quite easily – in corrosion layers for example (Thierry et al., 1988). The akaganéite spectrum has two bands at 725 and ca. 400 cm⁻¹ and that of feroxyhyte has bands at 655 and 400 cm⁻¹ (Bouchenit et al., 1989). Raman spectra of Fe oxides in rust are given in Thibeu et al. (1978). Bands for green rusts were observed at ca. 420 and 510 cm⁻¹ irrespective of the type of interlayer anion (Trolard et al. 1997; Genin et al. 1998). It has to be kept in mind that thermally unstable Fe oxides will eventually transform to anhydrous forms on long exposure to the laser beam (de Faria et al. 1997). In fact, 2-line ferrihydrite and schwertmannite were found to transform to hematite via maghemite, whereas 6-line ferrihydrite went to hematite directly. This was explained by the higher proportion of coordination-unsaturated Fe in the 2-line ferrihydrite rather than by the presence of structural ^{IV}Fe (Mazzetti & Thistlethwaite (2002). Raman spectroscopy has also shown that aspartate and glutamate adsorb on maghemite as inner sphere complexes (Rubim et al. 2001)

7.4

Ultraviolet-visible spectroscopy

7.4.1

General

The red and yellow iron oxides absorb strongly in the UV region and are weakly absorbing (strongly reflecting) in the visible/near IR regions. Extended optical spectra of the Fe oxides from the diffusely reflected radiation in the UV-VIS-NIR range of the electromagnetic spectrum (DRS) cover the range between ca. 200 and 1000 nm. These spectra reflect structural and other properties of the solids. They are the result of three types of electronic transitions: (1) Fe^{III} crystal or ligand field transitions, (2) interactions between magnetically coupled Fe^{III} ions and (3) ligand (oxygen)-metal charge transfer excitations from the O(2p) non-bonding valence bands to the Fe(3d)

ligand field orbitals or, in some cases, between Fe^{II} and Fe^{III} . Absorption in the visible range causes the vivid colours of most of the Fe oxides.

The *ligand field* (or d-d) transitions involve excitations from the ground state ${}^6\text{A}_1$ to the excited ligand field states¹⁾. These ligand field transitions are spin forbidden and so, at best, would be expected to be weak. In the iron oxides, however, their intensities are high owing to *magnetic coupling* of the next to nearest neighbour Fe^{III} in the crystal structure. This coupling can also lead to simultaneous excitation of two cationic centres by one photon, e.g. a $2{}^6\text{A}_1 \rightarrow \text{T, E}$ transition.

The *charge transfer* transitions – involving $\text{Fe}^{\text{III}}\text{-O}$ or $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ – are mainly responsible for absorption of visible light. They produce an absorption band centered in the near UV, one side of which (the *absorption edge*) extends into the visible region. This intense absorption is overlain by bands due to the ligand field transitions (between 550–900 nm) and double excitation processes at ca. 450 nm. The d-d transitions contribute more to the colour of iron oxides than would be expected, owing to the interactions between the $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ pairs.

Opaque minerals like iron oxides are frequently examined in the *reflectance* mode – and usually give diffuse reflectance spectra. Reflectance spectra provide information about the scattering and absorption coefficients of the samples and hence their optical properties. The parameters of reflectance spectra may be described in four different ways (1) by the tristimulus values of the CIE system (see 7.3.3); (2) by the Kubelka-Munk theory and (3) by using the derivative of the reflectance or remission function (Kosmas et al., 1984; Malengreau et al., 1994; 1996; Scheinost et al. 1998) and, (4) more precisely, by band fitting (Scheinost et al. 1999).

The Kubelka-Munk function ($f(r)$), the remission function, is often used to relate diffuse reflectance spectra to absorption and scattering parameters. This function is the ratio of the absorption, k , and the scattering, s , coefficient and is related to the diffuse reflectance, r , by

$$f(r) = \frac{(1-r)^2}{2r} = \frac{k}{s} \quad (7.1)$$

If, over the region of interest, the scattering coefficient hardly varies with wavelength, the shapes of the remission spectrum and the absorption spectrum should be very similar. The relationship between the remission function and the reflectance spectrum is shown in Figure 7.2 left, and the Kubelka-Munk functions of the different iron oxides are illustrated in Figure 7.2, right.

7.4.2

Spectra of the different Fe oxides

Figure 7.3-left shows diffuse reflection spectra of the different Fe oxides and Table 7.5 lists their transitions. Fig. 7–3 right summarizes the range of the crystal field band

- | | |
|--|--|
| <p>1) As the electron orbitals of the isolated Fe coordination polyhedra must be converted to the multielectron states found in the actual oxides,</p> | <p>the descriptions of the states of the oxides differ from those listed in Chapter 6.</p> |
|--|--|

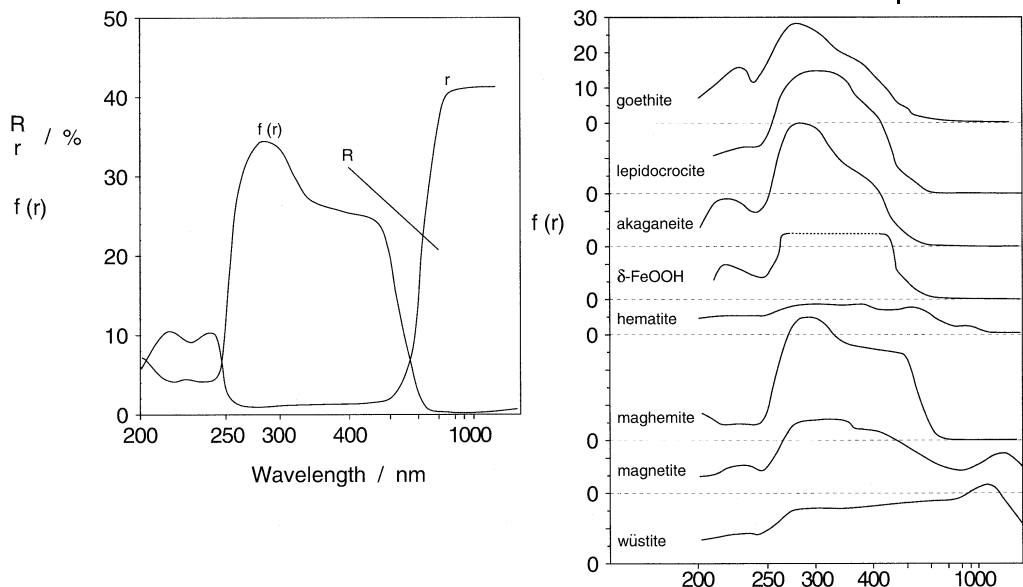


Fig. 7.2 Left: Relationships between diffuse reflectance (r), the specular reflectance (R) and Kubelka-Munk function ($f(r)$) of maghemite. Right: Kubelka-Munk function of various Fe oxides (Strens & Wood, 1979, with permission).

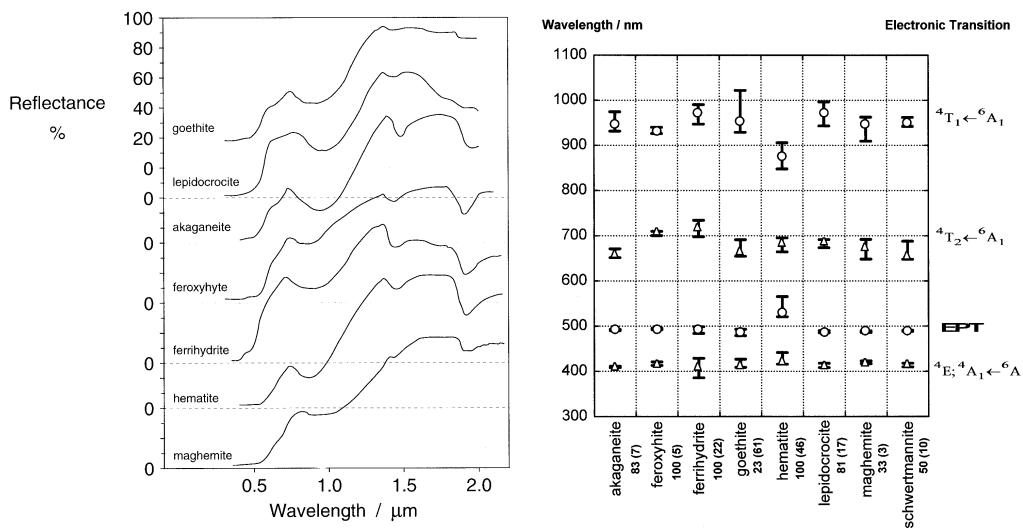


Fig. 7.3 Left: Diffuse reflectance spectra of Fe oxides in the UV-Vis-near IR range (Sherman et al., 1982, with permission). Right: Median and range of the crystal field band positions determined from second-derivative minima; the two

numbers below the mineral name are the per cent of correct classification of the various Fe oxide species by discriminant functions and in () the number of samples (Scheinost et al. 1998, The Clay Minerals Society; with permission)

Tab. 7.5 Ultraviolet-visible absorption bands and electron transitions for the iron oxides (data for magnetite, wüstite and akaganéite from Strens & Wood, 1979; with permission; bernalite from McCammon et al., 1995; remainder from Sherman & Waite, 1985; with permission)

<i>Oxide</i>	<i>Band position/nm</i>	<i>Transition/origin</i>
Goethite	917	${}^6A_1 \rightarrow {}^4T_1$ (4G)
	649	${}^6A_1 \rightarrow {}^4T_2$ (4G)
	480	$2({}^6A_1) \rightarrow 2({}^4T_1)$ (4G)
	434	${}^6A_1 \rightarrow {}^4E {}^4A_1$ (4G)
	364	${}^6A_1 \rightarrow {}^4E$ (${}^4D$)
	285	${}^6A_1 \rightarrow {}^4T_1$ (4P)
	250	$6T_{1u} \rightarrow 2t_{2q}$ charge transfer
	225	$1T_{2u} \rightarrow 2t_{2q}$ charge transfer
Lepidocrocite	961	${}^6A_1 \rightarrow {}^4T_1$
	649	${}^6A_1 \rightarrow {}^4T_2$
	485	$2({}^6A_1) \rightarrow 2({}^4T_1)$
	434	${}^6A_1 \rightarrow {}^4E$,
	359	${}^6A_1 \rightarrow {}^4E$
	304	${}^6A_1 \rightarrow {}^4T_1$
	239	$6T_{1u} \rightarrow 2t_{2q}$
	210	charge transfer
Akaganéite	908	${}^6A_1 \rightarrow {}^4T_1$
	502	$2({}^6A_1) \rightarrow 2({}^4T_1)$ (4G)
	290	charge transfer
	230	charge transfer
δ -FeOOH	880	${}^6A_1 \rightarrow {}^4T_1$
	330	
	217	charge transfer
Bernalite	885	${}^6A_1 \rightarrow {}^4T_1$
	625	${}^6A_1 \rightarrow {}^4T_2$
	431	${}^6A_1 \rightarrow {}^4E {}^4A_1$
Hematite	884	${}^6A_1 \rightarrow {}^4T_1$
	649	${}^6A_1 \rightarrow {}^4T_2$
	529	$2({}^6A_1) \rightarrow 2({}^4T_1)$
	444	${}^6A_1 \rightarrow {}^4E {}^4A_1$
	404	${}^6A_1 \rightarrow {}^4T_2$
	380	${}^6A_1 \rightarrow {}^4E$
	319	${}^6A_1 \rightarrow {}^4T_1$
	270	charge transfer
Magnetite	1400	charge transfer
	300	valence-band crystal field transition of the octahedral and tetrahedral cations

Tab. 7.5 (continued)

Oxide	Band position/nm	Transition/origin
Magnetite	934	${}^6A_1 \rightarrow {}^4T_1$
	666	${}^6A_1 \rightarrow {}^4T_2$
	510	$2({}^6A_1) \rightarrow 2({}^4T_1)$
	434	${}^6A_1 \rightarrow {}^4E, {}^4A_1$
	370	${}^6A_1 \rightarrow {}^4E$
	315	${}^6A_1 \rightarrow {}^4T_1$
	250	charge transfer
Wüstite	946	ligand field transition of octahedral Fe^{II}
	280	
	230	

positions and their median values found from second-derivative minima of 176 spectra of natural and synthetic Fe oxides (Scheinost et al. 1998). The following overview is based on this recent data. The second-derivative spectra of the iron oxides show four bands in the range from 350 to 1030 nm due to three single electron transitions: ${}^4T_1 \leftarrow {}^6A_1$ at 870–1030 nm, ${}^4T_2 \leftarrow {}^6A_1$ at 650–710 nm, and ${}^4E, {}^4A_1 \leftarrow {}^6A_1$ at 405–410 nm as well as the electron pair transition (EPT) at 488–493 nm. The latter determines the position of the absorption edge of the spectrum which is closely related to the colour of the oxide (see chap. 6.4). Thus, the position of this edge at 521–565 nm together with the band at 848–906 nm (${}^4T_1 \leftarrow {}^6A_1$) separates the red *hematite* from all other, more yellow Fe oxides (488–493 nm and 933–973 nm, resp.). The higher position of the EPT band of hematite is attributed to the face-sharing of the octahedra and the lower ${}^4T_1 \leftarrow {}^6A_1$ transition results from the lower crystal field splitting energy. *Ferrihydrite* and *feroxyhyte* can be separated from the rest by their ${}^4T_2 \leftarrow {}^6A_1$ transition which is positioned slightly above 700 nm as compared to the range of 655–687 nm for the other oxides (Sherman et al., 1982). The bands of ferrihydrite were broader than those of goethite, probably reflecting the difference in crystallinity.

The reflectance of *magnetite* in the UV-VIS-NIR range is very low due to a strong absorption band with a maximum at ca. 1500 nm. This band is caused by the presence of Fe^{II} and Fe^{III} in neighbouring octahedra between which electron hopping takes place. (Strens & Wood, 1979; Sherman & Waite, 1985; Sherman, 1987). *Wüstite* shows a sharp absorption band at 946 nm attributed to a d-d transition of octahedrally coordinated Fe^{II} . The strong absorption at 230 and 280 nm is due to crystal field transitions, but that at 400 nm and 1000 nm has not yet been assigned (Strens & Wood, 1979).

Based on these results, and in spite of considerable variation in the band positions of samples of the same Fe oxide, at least 80% of the pure akaganéite, feroxyhyte, ferrihydrite, hematite and lepidocrocite samples could be correctly classified by Scheinost et al. (1998) by discriminant functions based on the above four bands (Fig. 7.3 right) Magnetite could be identified by its band at 1500 nm, but for goethite,

maghemite and schwertmannite the discrimination was not reliable. In soils, only hematite and magnetite could unequivocally be distinguished from the other Fe oxides. Goethite and hematite could be quantified in synthetic mixtures of these two oxides, whereas for goethite and lepidocrocite mixtures and for ferrihydrite mixed with goethite and lepidocrocite, the differences in band positions were too small to be quantified (Scheinost et al. 1998).

The band positions of Fe oxides are also influenced by the *substitution* for Fe by other cations in the structure, as indicated partly by their colour. Scheinost et al. (1999) noticed a linear shift in the position of the ${}^6A_1 \rightarrow {}^4T_1$ transition from 943 to 985 nm and that of the ${}^6A_1 \rightarrow {}^4T_2$ transition from 653 to 671 nm for 47 synthetic goethites whose Al-substitution ($Al/(Al+Fe)$) ranged between 0 and 0.33 mol mol⁻¹ ($R^2 = 0.92$ for both). Mn^{III}-substituted goethites showed bands arising from Mn^{III} near 454 and 596 nm. The overall reflectivity in the visible range decreased as structural Mn increased from 0 to 0.20 mol mol⁻¹ (Vempati et al., 1995). The same effect has been observed for V^{III}-substituted goethites (Schwertmann & Pfab, 1994). The position of the EPT band of Mn^{III}-substituted hematite shifted to 545 nm and that of the ${}^6A_1 \rightarrow {}^4T_2$ transition to 700 nm (Vempati et al., 1995). The position of the same transition shifted from ca. 600 to 592 nm as the Al-substitution in hematite rose from 0 to 0.125 mol mol⁻¹ (Kosmas et al., 1986). *Crystal size and crystal shape* also have an effect on diffuse reflectance, as shown for hematite (see Fig. 6.12). As the crystals become smaller, reflectance increases and needles also reflect more than cubes, i.e. the colour becomes more vivid.

7.5

Mössbauer spectroscopy

7.5.1

General

Both Mössbauer spectroscopy and magnetometry are based on the magnetic behaviour of (essentially) iron in a crystal structure, but operate on different dimensional scales. Whereas Mössbauer spectroscopy yields information about charge and coordination, magnetometric methods are more sensitive to the type of magnetic coupling and to the magnetic domain status of particles.

The Mössbauer effect involves resonant absorption of γ -radiation by ${}^{57}\text{Fe}$ nuclei in solid iron oxides. Transitions between the $I = 1/2$ and the $I = 3/2$ nuclear energy levels induce resonant absorption (Fig. 7.4). A Mössbauer spectrum is a plot of the transmission of the rays versus the velocity of their source; movement of the source (${}^{57}\text{Co}$ for iron compounds) ensures that the nuclear environments of the absorber and the source will match at certain velocities (i.e. energies) and hence absorption takes place. In the absence of a magnetic field the Mössbauer spectrum consists of one (if the absorbing atoms are at a site of cubic symmetry) or two (symmetry distorted from cubic) absorption maxima. When a static magnetic field acts on the resonant nuclei, this splits the nuclear spin of the ground state into two and those of the ex-

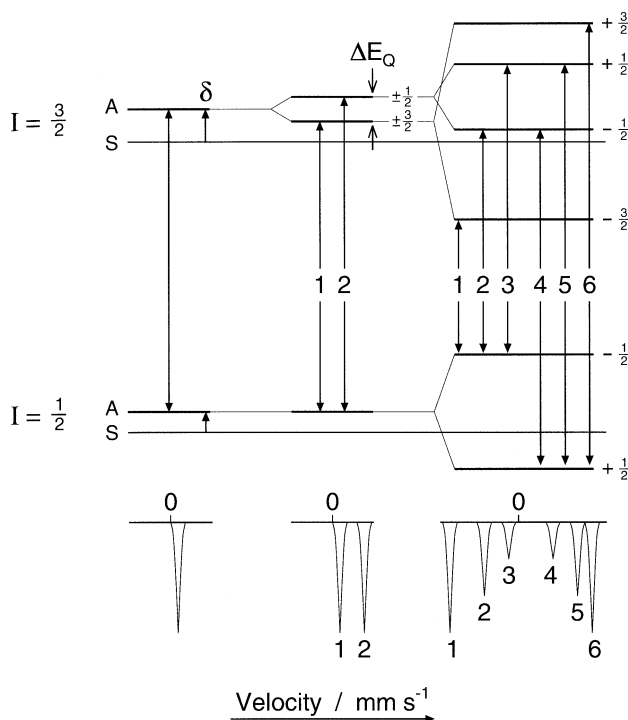


Fig. 7.4 Top: Nuclear energy levels of ^{57}Fe as shifted by electrical monopole (left), or as split by electrical quadrupole (center) or by magnetic dipole interaction (right), schematized for hematite at room temperature ($\delta > 0$ vs. $\alpha\text{-Fe}$, $E_Q < 0$, $B_{\text{hf}} 0$). Bottom: Schematic Mössbauer spectra corresponding to the energy levels schematized on top (J. Friedl, unpubl.).

cited state into four. The six allowed transitions then produce a 6-line spectrum (Fig. 7.5). The positions and the numbers of the absorption maxima are determined by the hyperfine interactions between the resonant nuclei and the electrons surrounding them. There are three types of hyperfine interaction:

1. The *electric monopole interaction* is a function of the s electron densities at the nucleus. This results in a displacement of the spectrum and is expressed as the velocity of the source (mm s^{-1}) necessary to counteract the displacement. This *isomer (or chemical) shift*, δ , provides information about the coordination number, the valency and spin state of the iron in the compound.
2. The *electric quadrupole interaction* is generated when an electric field gradient acts on the nucleus. The quadrupole interaction or splitting, ΔE_Q , provides information about the site distortion, e.g. by specifically bound ligands: it increases with increasing distortion.
3. The *magnetic hyperfine field*, B_{hf} (see Chap. 6), provides information about the valence and magnetic properties of the compound. Since the latter depend on temperature, Mössbauer spectra are often recorded at different temperatures, especially at

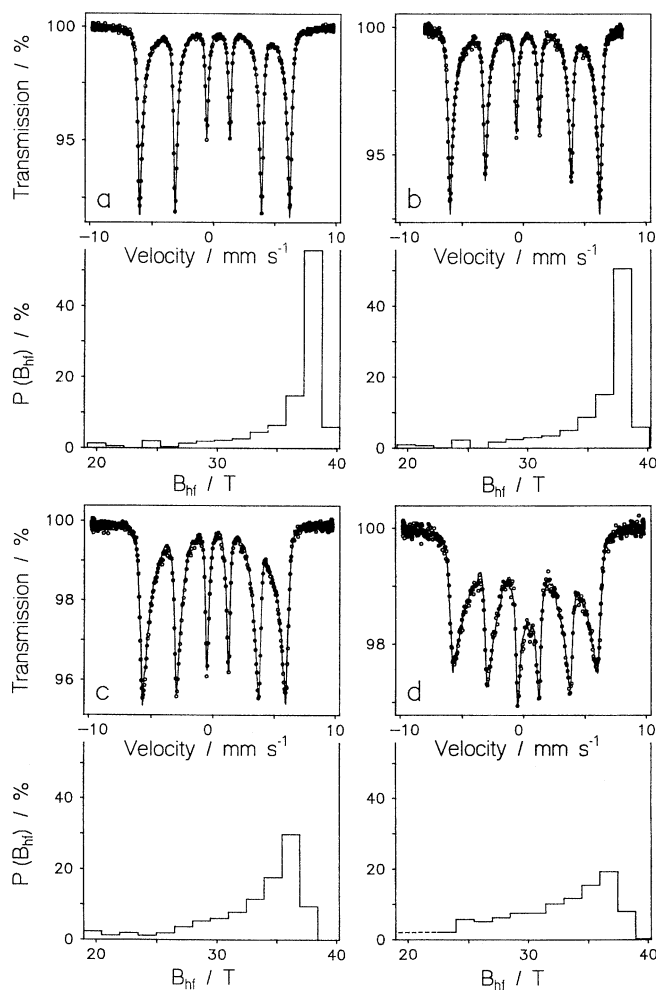


Fig. 7.5 Room temperature Mössbauer spectra and distributions of magnetic hyperfine fields for four goethites, decreasing in crystallinity from a to d (Murad, 1982a, with permission).

78K (liquid N₂) and 4.2K (liquid He) to induce magnetic ordering of those oxides which have a T_N below RT or are superparamagnetic at RT.

The absorption data are usually fitted with one or more doublets and/or sextets (Fig. 7.6) each with its own set of parameters (δ , ΔE_q , B_{hf}).

Mössbauer spectra are used for identification and characterization of Fe oxides. This follows primarily from the fact that the different Fe oxides order magnetically over a wide range of temperatures from 950 down to below 78K. The Mössbauer parameters of the various magnetically ordered Fe oxides differ considerably and thus allow unequivocal identification and often quantification in mixtures to be made. Mössbauer spectroscopy is insensitive to all isotopes except ⁵⁷Fe (and a few

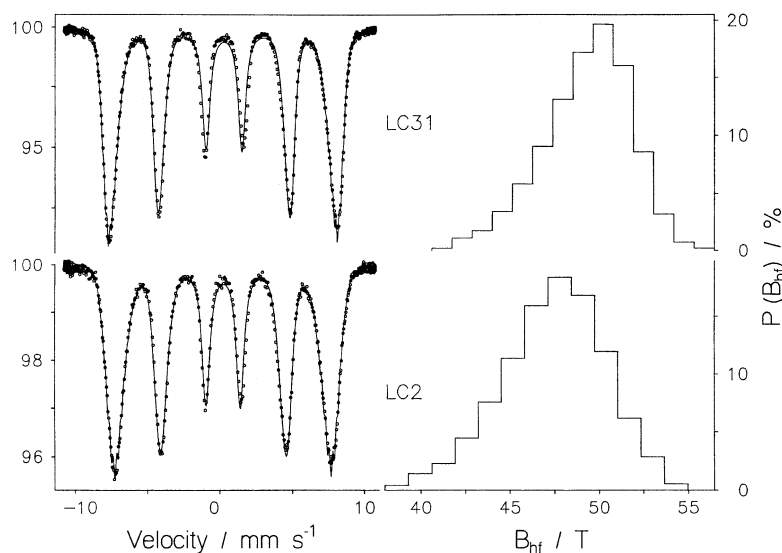


Fig. 7.6 Mössbauer spectra at 4.2 K and hyperfine field distributions of natural 6- (LC31) and 2-line (LC2) ferrihydrite from ferri-ferrous spring waters (Murad, 1988, with permission).

other rare elements) and this makes this technique particularly useful in systems where the iron oxides may be too low in concentration or in crystallinity to be detected by XRD, for example in soils, sediments, rust and organisms. Mössbauer spectroscopy also provides information about particle size and isomorphous substitution. In addition, application of an external magnetic field can help to distinguish ferrimagnetic phases from antiferromagnetic ones and may separate the two basic magnetic sublattices in poorly crystalline and in Al-substituted goethites; these are caused by an unequal distribution of Fe vacancies and of Al, respectively. Overviews are given by Murad, 1987;1990; 1996; Murad & Johnston, 1987; Meisel, 1989, 1996; De Grave et al., 1990, 1998; and Coey et al., 1991. The Mössbauer parameters of the iron oxides are summarized in Table 7.6.

Tab. 7.6 Mössbauer parameters for the iron oxides (RT-data mainly from Murad & Johnston, 1987; Murad, 1996; with permission)

Oxide	Recording temperature K	Isomer shift δ mm s^{-1}	Quadrupole splitting ΔE_Q mm s^{-1}	Hyperfine field B_{hf} T
Goethite	295	0.37	-0.26	38.0
	4.2	0.48	-0.25	50.6
Lepidocrocite	294	0.37	0.53	—
	4.2	0.47	0.02	45.8
	4.2	0.25	0.02	45.4 ^{g)}

Tab. 7.6 (continued)

Oxide	Recording temperature K	Isomer shift δ mm s^{-1}	Quadrupole splitting ΔE_Q mm s^{-1}	Hyperfine field B_{hf} T
Akaganéite	295	0.38	0.55	–
		0.37	0.95	–
	4.2	0.49	–0.02	48.9
			–0.24	47.8
			–0.81	47.3
Schwertmannite	295	0.39	0.64	–
	4.2	0.49	–0.37	45.6
δ -FeOOH	295	0.45	0.12	35
	4.2			52.5
HP FeOOH	480	0.03	–0.13	
	295	0.37	–0.13	35.2
	10	0.49	–0.118	47.2
Feroxyhyte	295 ^{d)}	0.37	–0.06	41
	4	0.48	~0	53
			~0	52
Ferrihydrite, 6-line	292	0.24	0.72	–
	4.2	0.25	–0.06	50
Ferrihydrite, 2-line	295	0.24	0.79	–
	4.2	0.24	–0.01	47
Bernalite ^{a)}	295	0.382	–0.006	43.1
	4.2		≤ 10.011	56.0 ^{e)}
Hematite	295	0.37	–0.197	51.75
	4.2	0.49	0.41	54.17
ε -Fe ₂ O ₃	295	0.21	–0.07	26.2
		0.38	–0.00	39.5
		0.39	–0.06	45.0
		0.37	–0.19	45.2
Magnetite	295	0.26	≤ 10.021	49
		0.67	0.00	46
Maghemite ^{b)}	295	0.23	≤ 10.021	50.0
		0.35		50.0
	4.2	0.40	≤ 10.021	52.0
		0.48	≤ 10.021	53.0
Wüstite	295	0.95	0.44	–
		0.90	0.79	–
Green Rust -SO ₄ ^{f)}	15	~1.3; ~0.5	~2.8; 0.4	–
Fe(OH) ₂ ^{g)}	300	1.05	2.98	
	4.2	1.4	3.06	~20 ^{d)}

a) Birch et al., 1993; **b)** da Costa et al., 1994a, b; **c)** Miyamoto, 1976; **d)** Madsen et al. 1985; **e)** De Grave et al. 1999; **f)** Refait et al. 1999; Fe^{II} Fe^{III}₂(OH)₁₂SO₄.nH₂O; **g)** Well crystalline natural sample from Schmiedeberg, Hesse; J. Friedl, pers. comm.

7.5.2

Spectra of the various Fe oxides**7.5.2.1 Goethite and Lepidocrocite**

The spectrum of well crystallized, (antiferromagnetic) *goethite* consists of a sextet with narrow lines and a B_{hf} of 38 T at room temperature, and of 50.6 T at 4.2 K. The RT spectrum may, however, appear as a doublet (super-paramagnetism, see Chap. 6) or may show the asymmetrically broadened lines of a sextet (Fig. 7.5); the latter result from a distribution of B_{hf} s owing to the poor crystallinity of the samples. Aluminium substitution lowers the T_N of goethite and as the T_N of the pure compound is close to RT, the RT spectrum of goethite is more sensitive to Al substitution than that of other iron oxides. Al substitution and/or poor crystallinity may modify the spectrum of goethite to such an extent that characterization (particularly for soil goethites) must be carried out at low temperatures, mostly at 77 or even 4.2 K. Increasing Al substitution and decreasing crystal size reduce the B_{hf} at 4.2 K (see eq. 3.2). The Mössbauer spectrum of paramagnetic goethite consists of a doublet with a quadrupole splitting of about 0.48 mm s^{-1} .

The very low Néel temperature (77 K) of *lepidocrocite* ensures that this compound is paramagnetic at RT. The Mössbauer spectrum at RT consists of a doublet with a ΔE_q of 0.53 mm s^{-1} . Magnetically ordered lepidocrocite shows a sextet with a B_{hf} of 45–46 T at 4 K that is lower than that of any other Fe^{III} oxide (Johnson, 1969; Murad & Schwertmann, 1984).

7.5.2.2 Ferrihydrite

Since synthetic and natural ferrihydrites are poorly ordered, nano-sized and often impure (natural samples), their Mössbauer spectra vary considerably. Both crystallinity (crystal size and order) and also interactions between the nano-sized particles play a role, the latter being affected by the drying procedure and –in natural samples– by impurities associated with the ferrihydrite particles. At room temperature, the maximum ΔE_q increases with decreasing crystallinity and a range between 0.62 and 0.86 mm s^{-1} , reflecting the variation in the symmetry of the $\text{Fe}^{\text{III}}\text{-O}_6$ -octahedra, has been recorded for various preparations (Murad, 1996). Depending, among other things, on particle size, magnetic ordering sets in between 70 and 130 K; it takes place over a range of temperatures rather than at a sharp transition temperature and comes to a completion only between ca. 45 and 10 K. At 4.2 K, the B_{hf} of a series of ferrihydrites with between 2 and 6 XRD-lines and produced uniformly at room temperature and pH 7 by varying the hydrolysis rate of Fe^{3+} , was invariant at 48.9 T. This may indicate that at 4.2 K, maximum magnetic order had been achieved irrespective of crystallinity (Schwertmann et al., unpubl.). Nevertheless, the spectral lines are broad and can only be fitted with parameter distributions which reflect a range of local Fe-environments. In contrast, impurities such as Si, Al, P, As and organics, may lower B_{hf} even at 4.2 K (Fig. 7.6). A 2-line ferrihydrite produced by thermal decomposition of a triacetato-hydroxy- Fe^{III} -nitrate complex had a particle size of $\leq 10 \text{ nm}$ and only 3.5% water and ordered magnetically between 90 and 120 K (Morris et al. 1991).

Ferrihydrites from ferritin also show a range of T_B s, depending on the source organism (human > limpet > bacterial) (Webb & St.Pierre, 1989) (see Fig. 17.3). The T_B of a 2-line ferrihydrite dropped from 50 to 25K when citrate was added at a level of citrate/Fe ~ 0.08 (Zhao et al. 1994). Particle interactions in aggregates also affect the Mössbauer parameters.

7.5.2.3 Hematite

At room temperature, the spectrum consists of a sextet with a ΔE_q of -0.20 mm s^{-1} and a B_{hf} of 51.8 T. The spectrum is less sensitive to the effects of Al substitution and poor crystallinity than that of goethite because hematite has a high Néel temperature (955K). The temperature of the Morin transition decreases linearly with $1/d$ (d = crystal size) from 260K for bulk hematite to down to ca. 200K for a crystal of a few tens of nm across. This relationship depends, however, on the way the hematite is synthesized (Vandenberghe et al. 2000). For example, a hematite with a particle size of $16 \pm 3 \text{ nm}$ prepared by heating Fe^{III} nitrate at 90°C in air for 20 days was superparamagnetic down to 230K, had a T_B of $143 \pm 5 \text{ K}$ and was weakly ferromagnetic at least down to 5 K (Bødker et al. 2000).

Increasing Al substitution and decreasing crystal size reduce the B_{hf} at RT (see eq. 3.9). The B_{hf} at 4.2K of the fraction not having passed the Morin transition was ca. 53T and essentially independent of Al substitution up to 0.1 mol mol^{-1} . In contrast, the B_{hf} at RT dropped from 51 to as low as 44T within the same range of Al substitution and the spectra were asymmetrically broadened. Heating these samples to 500°C raised B_{hf} to almost its original value. This shows that it is structural OH, reflecting Fe deficient sites, which causes the depression of B_{hf} (Dang et al. 1998; Schwertmann et al. 2000). As Al substitution and crystallinity are interrelated, their effects on the Mössbauer parameters can only be separated if the effect of crystallinity can be excluded by using well crystalline Al-hematites. DaCosta et al. (2001) achieved this by heating mixed Fe-Al-oxinates (see chap. 3). The B_{hf} of Si-containing hematites produced by heating Si-ferrihydrite to 800°C , decreased continuously from 51.65T to 51.16T as the Si/(Si+Fe) mole ratio of the ferrihydrite increased from 0 to 0.068 (Campbell et al. 2002). Poorly crystalline hematite with a B_{hf} at 4.2 K as low as 52.7 T was found in a hot brine deposit of the Red Sea (Schwertmann et al. 1998).

Paramagnetic hematite has a Mössbauer spectrum consisting of a doublet with a ΔE_q of 0.46 mm s^{-1} . The spectrum of superparamagnetic hematite (i.e. crystals < 8 nm) also consists of a doublet at RT, the ΔE_q of which increased with decreasing particle size up to as much as 1 mm/s . The ΔE_q of hematite is sensitive to pressure and changes sign at $> 3 \text{ GPa}$ (Vaughan & Drickamer, 1967). The high pressure form of hematite is characterized by a spectrum consisting of a doublet. A sextet is reported to form at pressures greater than 52 GPa (Syono et al., 1984).

7.5.2.4 Magnetite and maghemite

The Mössbauer spectrum of paramagnetic *magnetite* consists of one broad line which can be resolved into a component for the cubic A sites and a quadrupole split doublet for the B sites. Between the Curie and Verwey temperatures (see Chap. 6), magnetite is ferrimagnetic and the Mössbauer spectrum can be fitted with two sextets (Fig. 7.7),

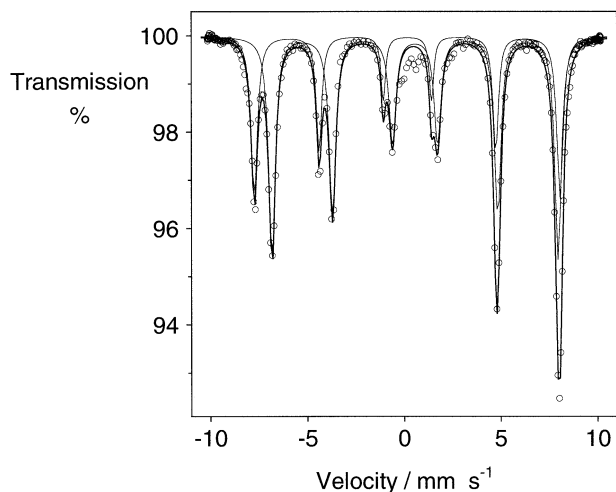


Fig. 7.7 Room temperature spectrum of magnetite fitted with two sextets (Murad, 1988, with permission)

one corresponding to high spin Fe^{III} on the tetrahedral sites ($B_{\text{hf}} = 49.2\text{T}$) and the other to $\text{Fe}^{2.5}$ on the octahedral sites. Electron dislocation causes the nucleus to sense one average valence ($B_{\text{hf}} = 46.1$). As usual, small particle sizes reduce the B_{hf} below that of the bulk material and broaden the resonance lines. The B_{hf} for both Fe^{III} and $\text{Fe}^{2.5}$ are slightly lower as Al enters the structure and the following relationship: $B_{\text{hf}} = 49.20 - 2.7z$, has been found for the substituted phase, $\text{Fe}_{3-z}\text{Al}_z\text{O}_4$: (Schwertmann & Murad, 1990). Below the Verwey temperature, the Mössbauer spectrum of magnetite is complicated, with components for each valence and crystallographic site; interpretation of such spectra is controversial.

Although the Fe^{III} of *maghemite* occupies two different sites in the structure, only one sextet appears at any temperature, indicating that the hyperfine parameters of both the A- and the B-sites are very similar; the two sextets corresponding to the A- and B-site are therefore hardly distinguishable, especially in well crystalline samples. The B_{hf} values for the two sites in maghemite produced by heating Fe-oxalate at 400°C were 50.0 and 50.1 T at 300 K and 51.6 and 52.9 T at 8 K (DaCosta et al. 1996). The 4.2 K spectrum also consists of two overlapping sextets with different isomer shifts. The two sextets were assigned to Fe^{III} in octahedral and tetrahedral positions (da Costa et al., 1994a). The RT spectrum of a maghemite ($a = 0.8432\text{ nm}$) formed by heating synthetic magnetite for 1355 h at 180°C showed two sextets with B_{hf} s of 49.1 and 46.4 T assigned to Fe^{III} on the tetrahedral and octahedral sites, respectively (Stanjek, 2000). Nano-sized, OH-containing maghemites formed by heating lepidocrocite or other OH-containing Fe oxides such as goethite and ferrihydrite at $3\text{--}400^\circ\text{C}$ in the presence of sugar (see chap. 14), could best be fitted with two sextets corresponding to B_{hf} s of ca. 45 and 49–50 T (Stanjek, 2000). The lowering effect of up to 0.66 mol mol^{-1} structural Al on B_{hf} at 80 and 300 K was demonstrated by Da Costa et al. (1996) (see chap. 2).

7.5.2.5 Other iron oxides

The spectrum of the magnetically ordered *akaganéite* is a sextet with asymmetric lines; this sextet consists of at least three components, the origins of which have not been conclusively established (Murad, 1979). Paramagnetic *akaganéite* produces a spectrum which consists of two doublets with different quadrupole splittings; the spectrum of the paramagnetic material grown in the presence of fluoride instead of chloride, includes a third doublet with a high quadrupole splitting of 1.33 mm s^{-1} (Chambaere et al., 1979). The Mössbauer spectrum of *schwertmannite* (Bigham et al., 1990; Schwertmann et al., 1995) shows an asymmetric doublet at RT which could be fitted with two quadrupole splitting distributions that have different isomer shifts reflecting two different Fe sites. The line width is considerably smaller ($\sim 0.5 \text{ mm s}^{-1}$) than that of the best crystalline ferrihydrite (0.71 mm s^{-1} for a one-doublet fit). Magnetic ordering is at 75 K. Since an external field did not induce magnetic ordering, the gradual transition can be interpreted as resulting from a range of Néel temperatures. The B_{hf} increases from 38.4 T at 50 K to 45.6 T at 4.2 K and is significantly lower than that of the most poorly crystalline ferrihydrite. The spectrum is again asymmetric and can only be fitted with two δ , ΔE_{q} and B_{hf} distributions. The low ordering temperature and the low B_{hf} reflect the presence of SO_4^{2-} as a structural component; this inhibits magnetic ordering.

Feroxyhyte is, owing to its poor crystallinity, superparamagnetic at room temperature with a spectrum consisting of a doublet with a ΔE_{q} of 0.69 mm/s . The spectrum at 4.2 K can be fitted by two sextets with two B_{hfs} (53.0 and 50.8 T) and two ΔE_{q} s (0.17 and 0.07 mm s^{-1}), but identical isomer shifts. The RT spectrum of *bernalite* was first fitted with two sextets and a weak doublet (Birch et al. 1993). The isomer shift at ca. 0.37 mm/s indicates that all Fe is trivalent and that only one Fe site is present. A 4.2 K spectrum gave a B_{hf} of ca. 56.0 T (De Grave et al. 1999a). The T_{N} is estimated from spectra between 80.5 and 350 K to be 427(5) K. It was concluded that magnetic ordering is of the weakly ferromagnetic type (McCammon et al. 1995).

As expected for a material with cubic sites, the RT spectrum of stoichiometric *wüstite* consists of a single line. The spectrum of the non-stoichiometric material shows an asymmetrically broadened doublet with contributions from Fe^{III} resonance and from two quadrupole split Fe^{II} doublets. The component peaks which contribute to this spectrum have not been fully resolved owing to the range of Fe^{II} environments in the structure (i.e. the variation in Fe content and vacancy level). At 77 K the Mössbauer spectrum consists of a broad doublet with contributions from Fe^{II} and Fe^{III} . $\text{Fe}(\text{OH})_2$ shows a sextet corresponding to a B_{hf} of 16.6 T at 20 K (Miyamoto, 1976; Genin et al. 1986) and to $\sim 20 \text{ T}$ at 4 K (Refait et al. 1999). The T_{N} is at 34 K (Miyamoto et al., 1967). The spectrum of *high pressure FeOOH* at room temperature consists of a sextet (Peret et al. 1973).

7.6

Magnetic properties (Magnetometry)

7.6.1

General

There is a number of magnetic properties (see Chap. 6) used to characterize the different Fe oxides. These properties were mainly developed in the frame of paleomagnetic studies in the geosciences (geophysics, geology and soil science), archaeometry, and material sciences. The most important properties are the type, strength and direction of the remanent magnetization. These can be used to identify the remanence carrier and the (magnetic) domain type of the particles viz. multidomain (MD), single domain (SD), pseudo single domain (PSD) and superparamagnetic (SP); usually, the particle size decreases in this order.

To induce magnetization the sample is exposed to an external magnetic field H_a and the magnetization, J , is recorded with a magnetometer. Starting from the original non-magnetic state where $J = 0$ at $H_a = 0$ (curve NC in Fig. 7.8), J first increases linearly with increasing H_a at low H_a , then non-linearly and finally reaches a maximum at high H_a ; this is the *saturation magnetization*, J_s when all magnetic moments of the sample are oriented in parallel. The slope of the initial, linear plot, J/H_a , is defined as the *initial magnetic susceptibility*, χ (see eq. (6.1) in 6.3.1). If at any point in the magnetization curve H_a is lowered, J will not become zero at $H_a = 0$; i.e. a hysteresis loop results (Fig. 7.8) from which the remanence magnetization, J_r , is derived. For ferrimagnetic materials, which can be saturated (as in Fig. 7.8), J_s is also called *saturation isothermal remanent magnetization*, SIRM. A field of

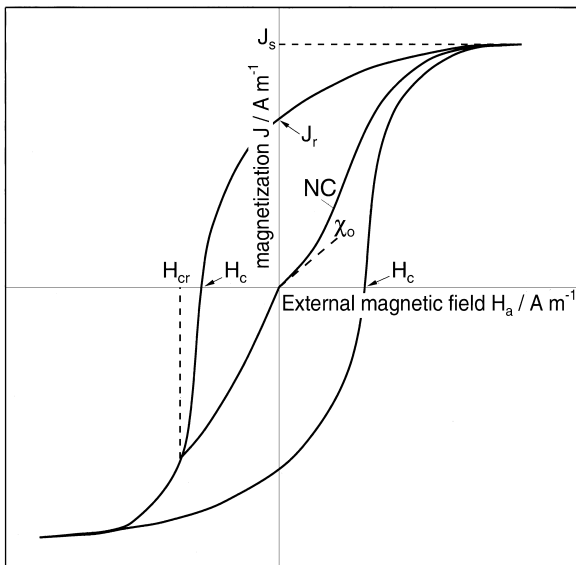


Fig. 7.8 Schematic presentation of the hysteresis loop.

strength H_{cr} is needed to remove the remanence. H_c , the magnetic field at which J_s becomes zero, is called coercive force or *coercivity*. Each type of magnetism shown in Figure 6.8 is associated with characteristic features which are displayed by the different Fe oxides.

7.6.2

Magnetic susceptibility χ

The specific mass magnetic susceptibility (m^3/kg) is very low for paramagnetic phases (e.g. olivine: $0.01-1.3 \cdot 10^{-6}$), slightly higher for the antiferromagnetic Fe^{III} oxides hematite, goethite and lepidocrocite ($0.3-1.7 \cdot 10^{-6}$) and very high for magnetite and maghemite ($4-20 \cdot 10^{-4}$). The two ferrimagnetic minerals will, therefore, dominate the magnetic behaviour of a sample and determine its susceptibility even at very low concentrations (some $mg\ kg^{-1}$).

As seen from the above ranges, the susceptibility is not a constant for a given phase, but depends on particle size and, hence, on domain type. χ shows a minimum near the border between SD – PSD type particles (Fig. 7.9). Qualitative information about the particle size distribution may be gained by measuring the susceptibility at two frequencies of the external magnetic field (e.g. at 470 and 4700 Hz). The relaxation time, τ i.e. the time for a spin reversal, is proportional to the product of particle volume and the anisotropy constant (see eq. (6.9) in Chap. 6). At lower frequencies, larger particles may still follow the alternating change of the external magnetic field; at higher frequencies, however, their contribution diminishes, and hence, τ decreases (Mullins & Tite, 1973). Experimental measurements show the percentage decrease of τ per order of magnitude of frequency is 1–20% for SP particles and <1% for SD and MD particles.

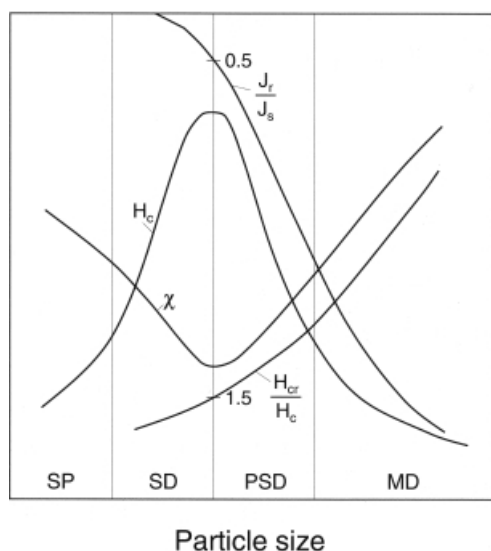


Fig. 7.9 Magnetic properties of small particles: H_c coercive force, susceptibility, J_r/J_s and H_{cr}/H_c (see Fig. 7.13) (modified from Soffel, 1991, with permission).

7.6.3

Magnetic anisotropy, coercivity and saturation magnetization

The application of higher fields to a sample gradually moves the Bloch walls¹⁾ or changes the directions of magnetization until a maximum magnetization is reached. The amount of energy (i. e. the coercive forces) necessary to achieve these changes is related to three different types of magnetic anisotropy.

The first type is the crystal *anisotropy* which is responsible for the dependence of the magnetization curves on the orientation of the crystal in the magnetic field. The energy E_k , which is necessary to deflect the magnetic moment in a single crystal from the easy direction into less easy ones is given for cubic crystals by:

$$E_k = K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) \quad (7.2)$$

with α referring to the cosine terms between the symmetry axes and the direction of magnetization and K_1 and K_2 being constants. Because $K_1 > K_2$, K_2 is usually omitted (see Tab. 6.5). In magnetite the “easy” direction of magnetization is [111], whereas [100] is the “hard” one, and [110] is intermediate (Fig. 7.10). In hematite, the easy direction is within the basal plane, where a weak ferromagnetism results from slight spin canting (see Chap. 6). The second type of anisotropy stems from the influence of particle shape and morphology on the coercive force. Particles with a rounded morphology (e.g. spheres) and equidimensional shape usually have smaller coercive forces than highly elongated or acicular particles. A third type of anisotropy

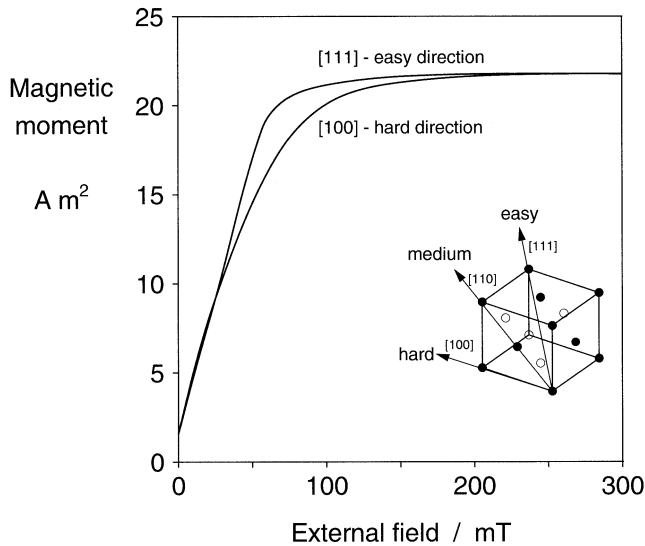


Fig. 7.10 Magnetization of magnetite single crystals.

1) In multidomain particles each domain is separated from another by the Bloch wall, where

the spin orientation changes gradually or abruptly.

Tab. 7.7 Maximum coercive force for natural single domain phases with different types of anisotropy and their critical diameter, d_{crit} , for the transition from single domain to pseudo-single domain type (from Soffel, 1991; with permission)

Mineral	Maximum coercive force, H_c/mT			$d_{crit}/\mu m$
	Shape	Stress [§] anisotropy	Crystal	
Goethite	0.5	250	1250	10–50
Hematite	1	600	500	10–30
Magnetite	150	12	30	0.03–0.1
TM60 [§]	50	150	30	0.5–1
Maghemite	125	15	30	0.03–0.1

§ Titanomagnetite $Fe_{(3-x)}Ti_xO_4$ with $x = 0.6$

\$ A strain of 50 MPa was assumed.

stems from relative contraction or dilation between the non-magnetized and the fully-magnetized state. This induces strain and a type of anisotropy called magnetostriction. It is dimensionless and ranges between 10^{-5} and 10^{-4} (see Tab. 6.5).

For all three types of anisotropy the *coercivity* can be calculated (Tab. 7.7). For SD magnetite and maghemite, shape anisotropy, dominates over strain and crystal anisotropy, whereas for hematite and goethite, morphology has little influence on coercivity.

The *saturation magnetization* of magnetite and maghemite is $80\text{--}100 \text{ Am}^2 \text{ kg}^{-1}$ and is thus two orders of magnitude higher than those of hematite or goethite (see Tab. 6.5). Neither goethite nor hematite can be magnetically saturated at the fields of 1–2 T which are usually available (Fig. 7.11).

7.6.4

Domain type

Whether a phase displays SD, PSD or MD behaviour, can be determined from the shape of its hysteresis loop. In MD particles the Bloch walls can be moved by lower energies than the directions of magnetization in SD particles. The hysteresis loops of MD particles, therefore, are much narrower than those of SD particles (Fig. 7.12). For ferrimagnetic phases, the ratios J_{rs}/J_s and H_{cr}/H_c (Fig. 7.9) (Day et al., 1977) can be used to distinguish between SD, PSD, and MD particles (Fig. 7.12, right). It should be kept in mind, however, that the coercive forces also depend on particle morphology. Calculations by Butler and Banerjee (1975) show that deviations from the rounded isometric shape towards elongated needles stabilize the SD behaviour and even SP particles may become SD (Fig. 7.13).

An alternative way of identifying the domain state of magnetite utilizes the dependence of both the crystal and strain anisotropy constants on temperature. K_1 of eq. (7.2) is negative at RT and becomes positive at $\sim 118 \text{ K}$, which is the so-called Verwey transition at which the crystal anisotropy vanishes and any original remanence, which is controlled by this anisotropy, is lost. This provides an easy test for the do-

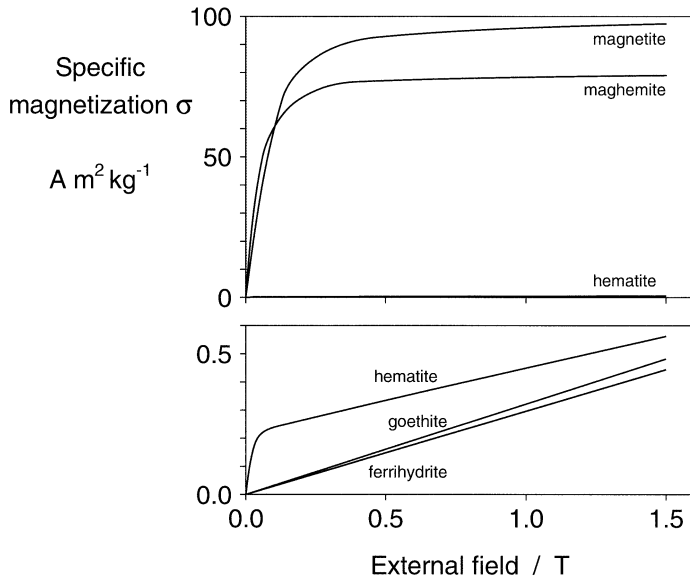


Fig. 7.11 Room temperature specific magnetization curves of magnetite, maghemite, hematite, goethite, and ferrihydrite (from Coey, 1988, with permission).

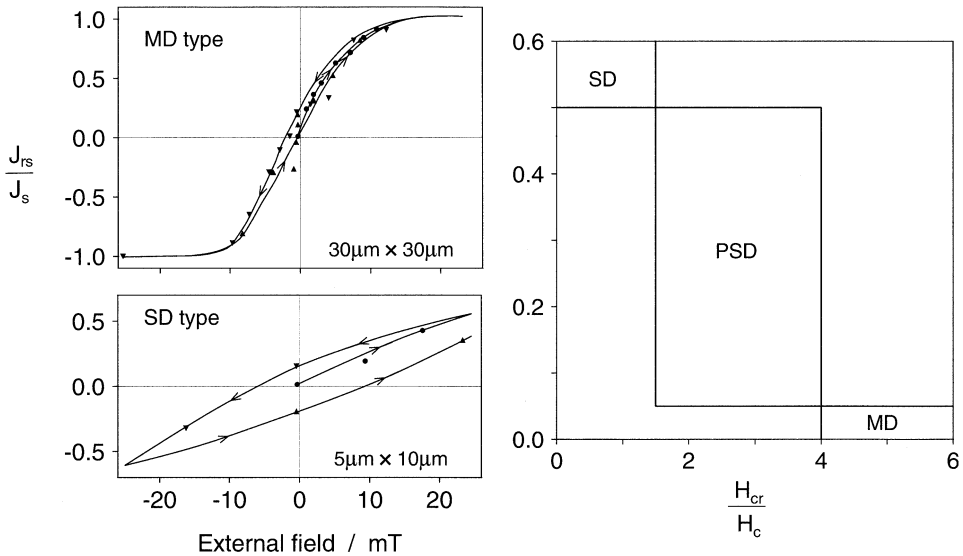


Fig. 7.12 Left: Hysteresis loops of MD (top) and SD magnetite (bottom) (modified from Dunlop, 1990, with permission). Right: The ratio J_{rs}/J_s as a function of the ratio of H_{cr}/H_c . The fields for single domain (SD), pseudo-single domain (PSD), and multi domain (MD) particles are given for magnetite.

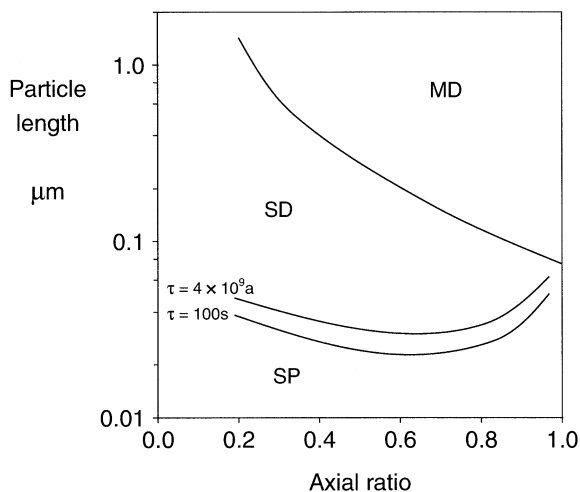


Fig. 7.13 The size and shape dependence of superparamagnetic (SP), multi-domain (MD) and single-domain particles (SD) as a function of the axial shape ratio. The times τ refer to relaxation times of $4 \cdot 10^9$ a and 100 s (from Butler & Banerjee, 1975, with permission).

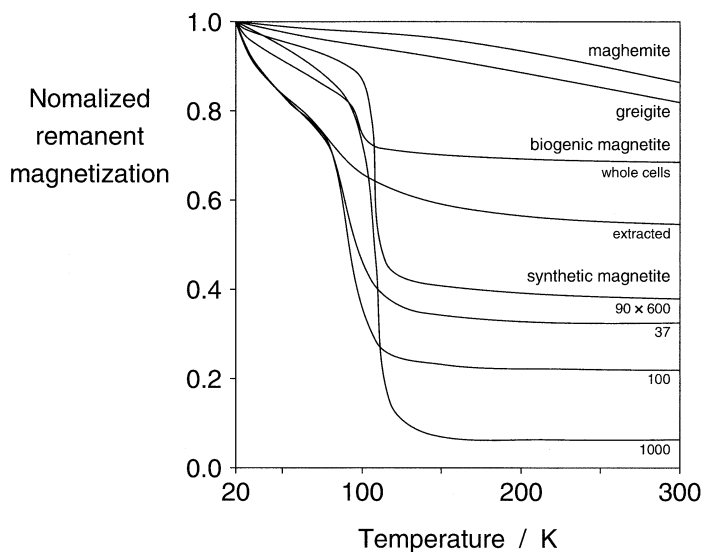


Fig. 7.14 Normalized decrease of the magnetization for magnetites of different origin. "Whole cells" refer to magnetotactic bacteria, "extracted" to biogenic magnetite extracted from these. The number indicates the size of synthetic magnetite crystals in nm (modified from Moskowitz et al., 1993, with permission).

main state; after saturating a sample at 20 K, the sample is heated from 20 K to 300 K while measuring the remanent magnetization, which is then normalized to that at 20 K (Fig. 7.14). MD particles lose almost all of their remanence (the more completely, the larger the particle), whereas with SD particles, where shape and/or stress anisotropy control the remanence, significantly less remanence is lost (see the

90 · 600 μm particles in Fig. 7.14). Since the Verwey transition is unique for magnetite, it can be used for distinguishing magnetite from maghemite or greigite, neither of which shows such a transition.

7.6.5

Curie temperature analysis

The disappearance of the magnetization above the Curie (or Néel) temperature (see Chap. 6) can be used to identify iron oxides. Thermal reactions – dehydration/dehydroxylation, oxidation/reduction – with accompanying phase transformations may give additional information about phases present. Therefore, not only the heating cycle, but also the cooling cycle is usually recorded to give the so-called $J_s(T)$ curve.

7.6.6

Applications

Ferrimagnetic phases are widely used for the storage of digital or analogue data on computer disks or audio tapes. Because known and mineralogically well-defined systems exist, magnetometric methods allow precise and specific characterization of these phases in order to control and improve their magnetic performance for technical applications.

Although widely used with geomaterials such as rocks and soils (Mullins, 1977) and as a tracer in genetic and environmental studies, the applicability of magnetometry (especially magnetic susceptibility) for identification and characterization of Fe oxides in *natural systems* is limited. Even though all Fe oxides contribute to χ and J , it is the ferrimagnetic oxides, magnetite and maghemite which, because of their much higher χ and J_s , determine these properties in any sample, even when present at very low concentrations. Hematite and goethite can be recognized by the positive slope of the magnetization curve at high fields (Fig. 7.11). The distinction between magnetite and maghemite can be made on the basis of the Verwey transition, which is present only in magnetite, or the $J_s(T)$ curve; maghemite transforms to hematite above 500 °C (see section 7.9), whereas, under reducing conditions, magnetite does not. The presence of lepidocrocite may show up in the $J_s(T)$ curve at about 200 °C due to the formation of maghemite (see section 7.10).

Difficulties arise, however, in mixtures and the magnetization curves will then depend on the proportions of the various oxides, including the antiferromagnetic ones (hematite, goethite) and on the crystal type (SD, MD). Positive identification is then only possible with the help of other methods, such as XRD (see for example Resende et al., 1986; Allan et al., 1988).

7.7

Other spectroscopic techniques

Other spectroscopic techniques used to characterize iron oxides are photoelectron (PS), X-ray absorption (XAS), nuclear magnetic resonance (NMR) (Broz et al., 1987), Auger (AES) (Seo et al., 1975; Kamrath et al., 1990; Seioighe et al. 1999), electron loss (EELS)), secondary ion mass (SIMS) and electron spin resonance (ESR) spectroscopy (Gehring et al., 1990, Gehring & Hofmeister, 1994) (see Tab. 7.8). Most of these tech-

Tab. 7.8 Techniques applied to examination of iron oxide surfaces

<i>Technique</i>	<i>Application</i>	<i>Feature</i>
Photoelectron spectroscopy (PES) 1. XPS 2. UPS	Composition	Photons in, electrons out
Auger electron spectroscopy (AES)	Composition	Electrons in, electrons out
Electron loss spectroscopy (EELS)	Composition	Electrons in, electrons out
	Energy states of adsorbed species	Electrons in, electrons out
High resolution electron loss spectroscopy (HREELS)	Identify adsorbed species	Electrons in, electrons out
Low energy electron diffraction (LEEDS)	Structure/long range atomic order	Electrons in, electrons out
Reflection high energy electron diffraction (RHEED)	Structure and composition	Electrons in, electrons out
Low energy ion scattering (LEIS)	Composition	Ions in, ions out
Secondary ion mass spectroscopy (SIMS)	Composition	Ions in, ions out
Small angle neutron scattering (SANS)	Vibrational states	Neutron in, neutrons out
Rutherford backscattering spectroscopy	Composition to a depth of some nm	He ⁺ in, He ⁺ out
X-ray absorption spectroscopy (XAS) 1. EXAFS 2. XANES	Local structure of surface and adsorbed species	X-rays in; electrons out
Electron spin (paramagnetic) resonance (ESR/EPR)	Chemical state of adsorbed species	Microwave technique in a magnetic field
Ellipsometry	Thickness and topography of oxide layers	Reflectance spectroscopy Involving polarised light
Scanning electron microscopy (SEM)	Topography	Electrons in, electrons out
Transmission electron microscopy (TEM/HRTEM)	Topography	Electron microscope
Scanning tunnelling microscopy (STM)	Composition/topography and atomic structure	Tunneling current scans a conducting surface
Atomic force microscopy (AFM)	Structure, topography force measurements	Commonly involves tip/sample repulsion

niques have been used to determine the composition of the oxides and/or to study the nature of adsorbed species on the oxide surface. Full details of these techniques as applied to oxide surfaces are given in Hochella (1988, 1990, 1995), Brown et al. (1989), Brown (1990) and Stipp (1994).

Photoelectron and X-ray absorption spectroscopy have been most widely applied to iron oxides to date, although an increasing number of new techniques is being investigated; frequently a combination of methods has been used. EELS has been used for chemical analysis of thin Fe oxide particles from an aquatic system (Mavrocordatos & Perret, 1998). This technique was also used in conjunction with TEM and convergent beam electron diffraction (CBED) to measure the thickness of hematite platelets up to 400 nm in thickness (Nishino et al. 1998). Auger spectroscopy has shown that upon heating magnetite films at 427 °C, Mg from the MgO substrate diffused into the Fe oxide film (Ruby et al. 1999). Rutherford back scattering (RBS) also showed that heating promoted diffusion of Mg into the magnetite (Thevuthasan et al. 2000). ESR applies to paramagnetic ions and provides information about coordination, oxidation state and mechanism of adsorption. It was used to show that Mn^{II} adsorbed on goethite as clusters (Bleam & McBride, 1985).

7.7.1

Photoelectron spectroscopy

Photoelectron spectroscopy involves detection and analysis of the photoelectrons produced by interaction of radiation with a solid. This radiation may be X-rays (for X-ray photoelectron spectroscopy, XPS or ESCA) or ultraviolet radiation (UPS); it causes the removal of a single core or valence electron, respectively. The kinetic energy, E_k , of these electrons is given by the following equation:

$$E_k = h\nu - E_B - \Theta_{sp} \quad (7.3)$$

where E_B is the binding energy of the ejected electron and is greater than the photon energy ($h\nu$) and Θ is the work function of the spectrophotometer. The kinetic energy is measured using a spectrophotometer and a spectrum obtained by plotting the measured photoelectron intensity as a function of the binding energy. Each element has its own characteristic set of binding energies and, hence, spectral lines, which can be correlated with atomic orbital energies. For the iron oxides the $\text{Fe}(2p_{3/2})$ and $(2p_{1/2})$ lines and the $\text{O}(1s)$ line are most commonly scanned (Brundle et al., 1977; Harvey & Linton, 1981; Wandelt, 1982). The main use of this technique for the iron oxides is to provide information about the oxidation and structural state parameters and to determine the surface composition to a depth of less than 10 nm. PES spectra are shown in Figure 7.15. XPS spectra of the (010) cleavage face of two very well-crystalline natural goethites from Cornwall and Colorado gave peak maxima for $\text{Fe}(2p_{3/2})$ at 711.5 ± 0.1 eV and for $\text{O}(1s)$ at 531.3 ± 0.1 and 530.0 ± 0.1 eV (Rakovan et al. 1999). Except for goethite, the $\text{O}(1s)$ peak does not vary for the different iron oxides and the Fe peaks are so closely spaced (Tab. 7.9) that differentiation between oxides in a mixture (e.g. rust) is difficult. The use of these spectra as an identification tool

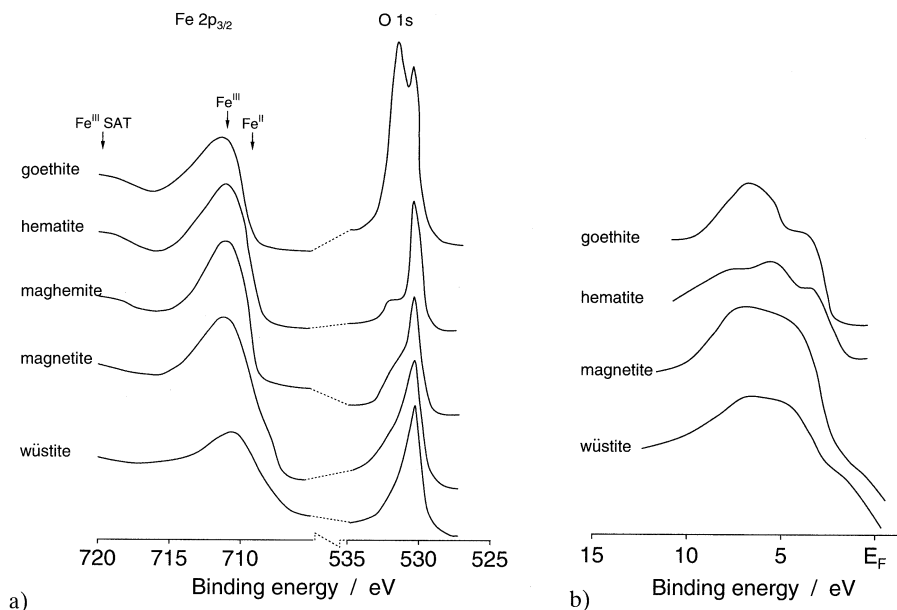


Fig. 7.15 a) Fe(2p_{3/2}) and O(1s) XPS spectra of various iron oxides and b) valence band spectra of their surfaces (Brundle et al., 1977, with permission).

Tab. 7.9 Binding energies (eV) of major core lines in iron oxides

Oxide	Fe(2p _{3/2})	Fe(3p _{3/2})	Fe(3s)	O(1s)
Goethite	711.9	56.6	94.2	530.3
Ferrihydrite	711.6	—	—	530.9
Hematite	711.0	55.7	93.6	529.8
Magnetite	708.3	53.9	—	530.2
Maghemite	711.0	55.7	93.6	530.0
Wüstite	709.5	54.9	92.5	530.0

Data from Harvey & Linton (1981); McIntyre & Zetaruk (1975); Wandelt (1982) Rakovan et al. (1999)

is, therefore, limited.. The technique is useful for investigation of adsorbed species on oxide surfaces. For silicate at the surface of ferrihydrite, the Si(2p) XPS peak was shifted to 100.9 eV as compared to that of amorphous SiO₂ (102.8 eV) (Vempati et al., 1990). Glasauer et al. (2000) interpreted the shift of the Si(2s) peak from 154.4 (quartz) to 153.3 eV in coprecipitated Si-ferrihydrite (Si/(Si + Fe) = 0.11) as evidence of a Si-O-Fe bond. XPS suggested that adsorption of phosphate, sulphate and selenite on goethite involved bonding to two singly coordinated Fe-OH groups per anion (Martin & Smart, 1987). XPS was also used to monitor the adsorption of zinc on fer-

rihydrite (Harvey & Linton, 1984). XPS spectra were used in combination with AFM and RBS to characterize the morphology, stoichiometry and chemical state of hematite films prepared by ion beam induced, chemical vapour deposition (Yubero et al. 2000) and the chemical environment of magnetite and wüstite thin films (Ruby et al. 1999). In combination with ion scattering spectroscopy (ISS), XPS spectroscopy showed that thin films of hematite grew on a SiO_2 substrate as islands, whether they were deposited at room temperature or annealed at 500°C (Yubero et al., 2000a).

7.7.2

X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) comprises two parts which provide complementary information. These are *X-ray absorption spectroscopy near edge structure* (XANES) and *extended X-ray absorption fine structure* (EXAFS) spectroscopy. Synchrotron radiation is used to photo-ionize the core electrons of a target atom. Absorption spectra are collected by continuously increasing the energy of the incident photons. As soon as the energy is high enough to eject the core electrons, the absorption abruptly increases (absorption edge). With increasing oxidation state, the absorption edge shifts to higher energies (ca. 1–2 eV per step), thus the valence can be determined. The outgoing electrons are backscattered by neighbouring atoms and interference of these backscattered electrons with the outgoing ones produces a fine structure in the spectrum at energies greater than the absorption edge; this is the EXAFS spectrum (Brown et al. 1988; Fendorf & Sparks, 1996). EXAFS spectra reflect the local environment around the photo-ionized atoms and so provide information about the number (z) and identity of nearest and next-to-nearest neighbours, and their interatomic distances. The Fourier transform of the absorption spectrum gives a radial distribution function (RDF) which shows a series of peaks at different interatomic distances. The heights of the peaks are proportional to the number of scattering atoms at any particular distance and the peaks themselves, are associated with the shells of the atoms which surround the central atom.

Most of the initial EXAFS work on structural aspects of the iron oxides has been carried out by Manceau and co-workers (Manceau & Combes, 1988; Combes et al., 1989, 1990; Charlet & Manceau, 1992a; Manceau & Drits, 1993; Charlet & Manceau, 1993); they produced low temperature EXAFS spectra at the Fe-K edge at 1.85 GeV and 300–260 mA. These workers were concerned initially with the identification and structural characterization of hematite, ferrihydrite and the different polymorphs of FeOOH (see Fig. 2.3). They also followed the stages in the transformation of ferrihydrite to more crystalline phases. EXAFS was used to identify a poorly ordered Fe oxide (ferrihydrite?) in rusts formed under a range of conditions on an Fe-3%Si alloy (Suzucki, et al. 2001). In addition, EXAFS is being increasingly used to characterize adsorbates on Fe oxide surfaces (Manceau et al. 1992, 2000; and see chap. 11). As EXAFS is most suitable for heavy elements, it has been applied mainly to adsorbed cations (particularly those of toxic elements) and to oxyanions of Se, Cr and As. O'Day et al. (2000) point out that care is necessary in interpreting these EXAFS data from strongly hydrated surface complexes.

XANES spectra provide information about contaminants present at too low a level to produce EXAFS spectra. It has been used to investigate the oxidation of As^{III} on Mn-goethite (Sun et al. 1999). This technique has also provided information about the valence of Fe in Fe oxide films during cathodic reduction in a borate buffer (Schmicki et al. 1996), about the dissolution of Fe oxide films in acidic solutions (Virtanen et al. 1997) and about the orientation of styrene molecules adsorbed on FeO (111) and Fe₃O₄ (111) (Wuehn et al. 2000).

7.8

Diffraction

7.8.1

X-ray diffraction

X-ray diffraction (XRD, Brown, 1980) involves interaction of electromagnetic radiation with a wavelength (λ) of around 0.1 nm, with the atoms in the solid. As the distances between the atoms in a crystal structure are comparable with the wavelength of the radiation, crystals can diffract X-rays. In certain directions (angles of incidence, θ) the elastically scattered rays interfere constructively, thus leading to enhanced intensity. These angles, θ , the wavelength of the rays and the lattice spacings (d_{hkl}) are related by the Bragg equation

$$n\lambda = 2d_{hkl} \sin \theta \quad (7.4)$$

The X-ray diffraction pattern of a powdered phase is a plot of the observed diffraction intensity against the Bragg angle, θ . Depending on the interference conditions each atom plane produces a series of n reflections. From these patterns the interplanar spacings (d_{hkl} values) can be calculated using the Bragg equation. Each compound has its own characteristic set of d values and intensities which can be used for identification. The interplanar spacings and their relative intensities for each iron oxide are listed in Table 7.10. X-ray patterns are obtained using diffractometers and the diffractograms can be fitted using the whole-diffractogram procedures of the Rietveld analysis (Izumi, 1993).

Typical X-ray diffraction patterns of the Fe^{III} oxides are shown in Figure 7.16. They provide the three parameters, namely line (angle) position, width and intensity from which the nature of the oxide, its quantity (in a mixture), its unit cell parameters and its crystallinity (crystal size and order) can be deduced. The crystal structure of unknown compounds may also be determined. XRD is still the most reliable way to identify a particular oxide because it is based on the long range order of the atoms, whereas most other methods (e.g. Mössbauer spectroscopy, EXAFS) characterize the atoms and their immediate (short range) environment.

Deviations from the unit cell parameters obtained from an X-ray diffractogram of a pure phase may be used to quantify the extent of Fe substitution by other cations, provided the ionic radius of these foreign cations differs sufficiently from that of

Tab. 7.10 (continued)

Goethite <i>contd.</i>	Lepidocrocite <i>contd.</i>						Ferrihydrite <i>contd.</i>
0.13936 3 303	0.1203 11 022						0.1724 1
0.13694 2 013	0.11914 7 1010						0.1529 5
0.13590 3 701	0.11845 7 131						0.1472 6
0.13459 1 602	0.11814 7 222						
0.13173 3 321	0.11781 4 612						
0.12921 <1 420	0.1096 1 802						
0.12654 1 313							

Tab. 7.10 (continued)

Hematite 34–664			Magnetite 19–629			Maghemite 25–1402			Wüstite 6–615			ϵ -Fe ₂ O ₃ ⁵⁾ 33–646			Bernalite ⁶⁾			Green rust I ²⁾			Green rust II ²⁾			Fe(OH) ₂ ⁷⁾					
d nm	I	hkl _{hex}	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl	d nm	I	hkl
0.3684	30	012	011	0.4852	8 111	0.590	6 110	0.3784	100	0.802	vs	003	1.092	vs	001	0.4597	vs	0.3684	100	0.3784	100	0.802	vs	003	1.092	vs	001	0.4597	vs
0.2700	100	104	211	0.2967	30 220	0.482	6 113	0.2153	100 200	0.2981	35 –411	0.2676	15	0.401	v	006	0.548	s	0.2676	15	0.401	v	006	0.548	s	002	0.2817	s	
0.2591	70	110	101	0.2532	100 311	0.373	6 210	0.1523	60 220	0.2728	100 –411	0.2393	16	0.2701	m	102	0.365	s	0.2393	16	0.2701	m	102	0.365	s	003	0.2403	vs	
0.2207	20	113	210	0.24243	8 222	0.340	7 213	0.1299	25 311	0.2548	20 040	0.2185	15	0.2701	m	104			0.2185	15	0.2701	m	104						
0.18406	40	024		0.17146	10 422	0.373	6 210	0.1243	15 222	0.2458	30 023	0.2023	6	0.2408	m	105	0.2747	m	0.2023	6	0.2408	m	105	0.2747	m	004	0.1782	s	
0.16941	45	116	321	0.16158	30 511	0.340	7 213	0.1077	15 400	0.2243	20 –512	0.1892	10			107			0.1892	10			107			100			
0.15992	10	018	332	0.14845	40 440	0.295	30 220	0.0988	10 331	0.2176	14 521	0.1692	17	0.2037	w	108	0.2660	ms	0.1692	17	0.2037	w	108	0.2660	ms	101	0.1629	s	
0.14859	30	214	310	0.12807	10 533	0.2514	100 313	0.0963	15 420	0.1855	12 –622	0.1545	9	0.1598	mw	101	0.2459	ms	0.1545	9	0.1598	mw	101	0.2459	ms	102	0.1535	m	
0.14538	30	300	211	0.10930	12 731	0.2086	15 400			0.1735	25 720					110							110			003			
0.13115	10	1010		0.10496	6 800	0.1701	9 426			0.1666	25 352			0.1567	mw	113	0.2195	ms	0.1666	25 352			0.1567	mw	113	0.2195	ms	005	
0.13064	6	119		0.09695	6 751	0.1604	20 513			0.1537	12 –723			0.1487	w	116	0.1938	ms	0.1537	12 –723			0.1487	w	116	0.1938	ms	103	
0.12592	8	220		0.08802	6 931	0.1474	40 440			0.152	35 262								0.152	35 262						103	0.201		
0.11896	5	128		0.08117	6 951	0.1318	6 620			0.1469	30 552								0.1469	30 552						104	0.1067	wd	
0.11632	5	0210								0.1416	10 –832																210		
0.11411	7	134								0.1272	8 539								0.1272	8 539						203	0.1040	m	203
0.11035	7	226								0.1204	5 441								0.1204	5 441						211			
0.10557	7	2110								0.1115	6 646								0.1115	6 646						110	0.0968	md	212
0.09606	5	324								0.1086	10 733								0.1086	10 733						111	0.0941	md	114
0.09516	5	410								0.1043	7 800								0.1043	7 800						300			
0.09081	5	1310								0.0983	5 826								0.0983	5 826						112	0.0923	w	005
0.08789	6	416								0.0963	8 753								0.0963	8 753						301			
0.08436	5	1214																											

1) Bigham et al. 1994; 2) Bernal et al. 1959; 3) Carlson & Schwerdtmann, 1980; 4) Chenavas et al., 1973; 5) Dezsi & Coey, 1973; 6) Birch et al. 1993; 7) Miyamoto, 1976

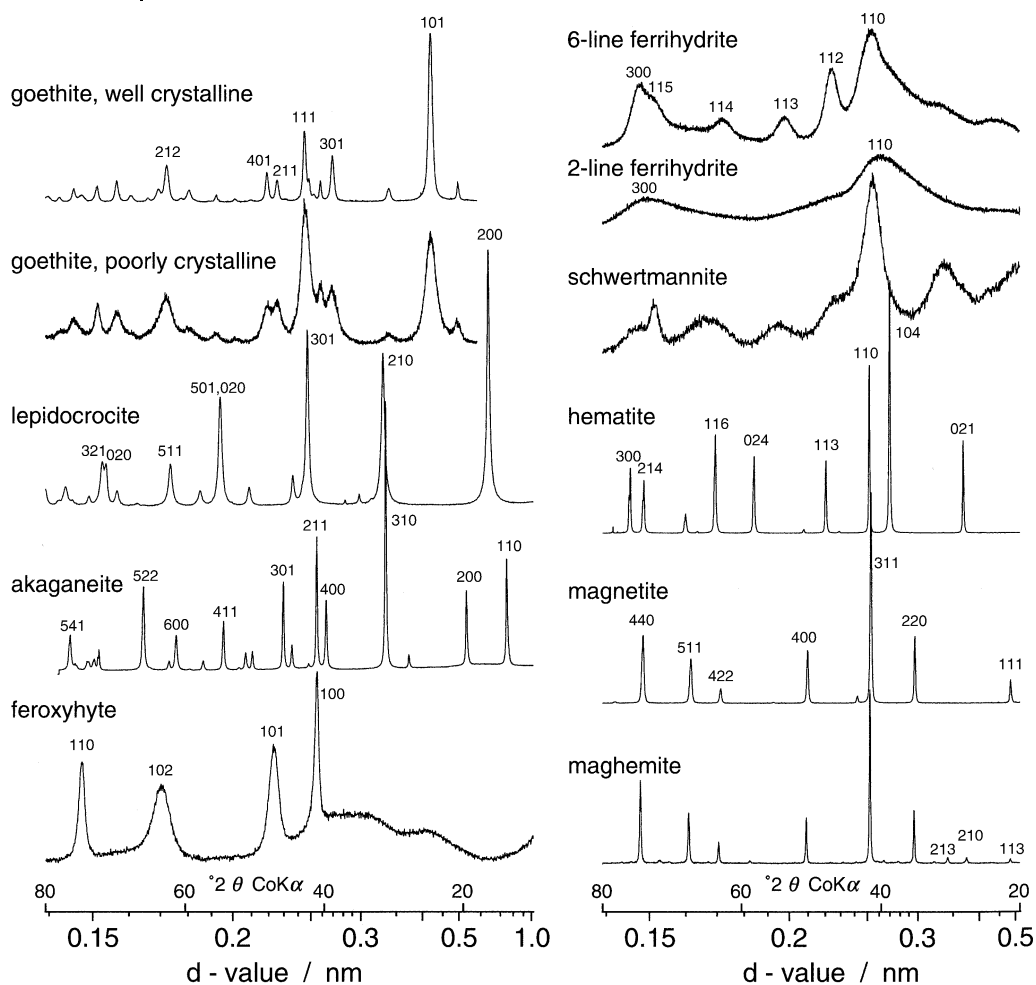


Fig. 7.16 X-ray powder diffractograms of Fe^{III} oxides.

Fe^{III} and the level of substitution is not too low (see Chap. 3). If the crystals are small (<100 nm) and/or show structural strain (disorder), the broadening of the reflection is greater than that due to instrumental broadening. Differences in broadening of various reflections are due to different degrees of development of small crystals in various directions, hence they provide information about crystal shape. For example, platyness of very small hematite crystals (<100 nm) is reflected by broad hkl and sharp hk0 lines (Schwertmann et al., 1977; Duvigneaud & Derie, 1980). The relative intensities given in Table 7.10 are only observed if the crystals are randomly oriented within the sample. An-isodimensional particles (plates, rods) tend to show preferred orientation and this changes the relative intensities of the peaks. From such changes information about the shapes of Fe oxide crystals can also be obtained (Schwert-

mann et al., 1968). The diffractogram of the cubic form of maghemite is identical to that of magnetite with some line shift towards higher angles, whereas the tetragonal form displays additional X-ray lines indicating a superlattice.

7.8.2

Other Diffraction Techniques

Like X-ray diffraction patterns, neutron and electron diffraction patterns provide averaged information about the structure of a compound. Details of these techniques are given in works by Hirsch et al. (1965) and West (1988). *Neutron diffraction* involves interaction of neutrons with the nuclei of the atoms. As the neutrons are scattered relatively evenly by all the atoms in the compound, they serve to indicate the positions of the protons in an oxide hydroxide. This technique has been applied to elucidation of the structure and/or magnetic properties of goethite (Szytula et al., 1968; Forsyth et al., 1968), akaganéite (Szytula et al., 1970), lepidocrocite (Oles et al., 1970; Christensen & Nørnlund-Christensen, 1978), hematite (Samuelson & Shirane, 1970; Pernet et al., 1984) and wüstite (Roth, 1960; Cheetham et al., 1971; Battle & Cheetham, 1979). A neutron diffractogram of a 6-line ferrihydrite was recently produced by Jansen et al. (2002) and has helped to refine its structure (see chap. 2).

Electron diffraction results from scattering of electrons by both the electrons and the nuclei of the compound. The electron diffraction pattern can, unlike that of X-rays or neutrons, be related to an image of a crystal, thus enabling the composition of a particular region to be investigated. An advantage is that as electrons are scattered more efficiently than X-rays, shorter exposure times (minutes) are required. In addition, comparatively small samples and even single crystals can be examined (selected area electron diffraction, SAED) and the electrons can be focussed with magnetic lenses and the beam tilted, thus permitting flexibility in examination. On the other hand, as electrons do not penetrate matter as easily as X-rays, only relatively thin samples (50–100 nm) can provide an electron diffraction pattern. Figure 7.17 shows electron nano diffraction patterns for a extremely poorly ordered (2-line) ferrihydrite (Janney et al. 2000).

Whereas electron diffraction is used to investigate the bulk material, the atomic structure of the surface is studied using low energy electron diffraction (LEED). This technique involves interaction of low energy electrons with the surface; the scattered electrons undergo Bragg diffraction and produce a diffraction pattern from which unit cell size and shape may be determined. The LEED pattern from a cleaved (001) hematite surface indicated a slightly distorted, close packed anion sheet with the Fe atoms uniformly distributed over $\frac{1}{6}$ of the available sites and located in oxygen triplets (Hochella et al., 1989). LEED has been used to investigate the structural transformation undergone by the hematite surface upon heating. The (001) hematite surface undergoes a stoichiometric 2×2 reconstruction upon heating to 700 °C in vacuo (Kurtz & Heinrich, 1983). Ar^+ ion bombardment followed by annealing in 10^{-10} torr O_2 at 900 °C induced a 1×2 reconstruction of the (102) surface (Lad & Heinrich, 1988). A combination of LEED, Auger spectroscopy and XPS identified the epitaxial film deposited on a platinum substrate as magnetite (Barbieri et al., 1994). The same

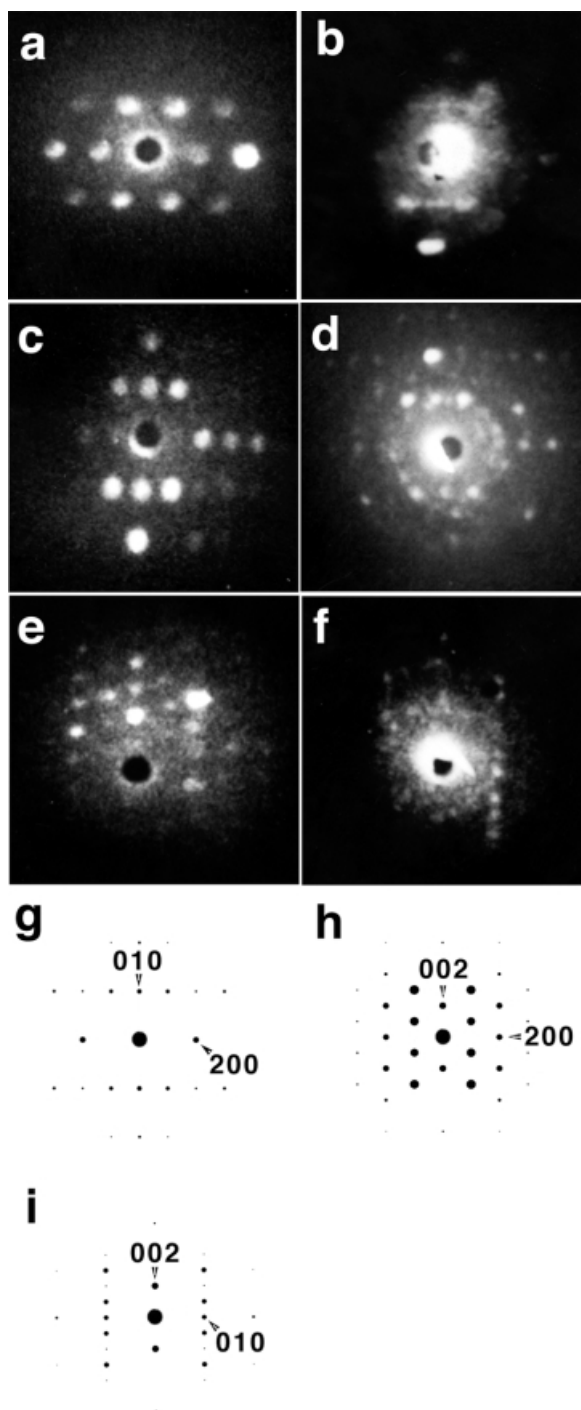


Fig. 7.17 Electron (nano) diffraction pattern from the double-chain structure of 2-line ferrihydrite with the beam considered to be parallel to $[001]$ (a–d), $[010]$ (e) and $[100]$ (f); respectively (Janney et al. 2000; with permission).

study showed that prolonged annealing of a hematite single crystal transformed the surface to a strongly relaxed magnetite (111) surface with $\frac{1}{4}$ monolayer of Fe ions distributed over an hcp oxygen layer. LEED, in conjunction with STM, AES and thermal desorption spectroscopy, has been used to examine the surface structures of well crystalline films of magnetite (111), hematite (001) and wüstite (111): these films were being investigated as models for the catalytic dehydrogenation of ethyl benzene to styrene (Shaikhutdinov et al. 1999 and references therein).

A combination of LEED, AES and STM showed that well ordered, potassium doped surfaces are formed by depositing K on the magnetite (111) plane followed by annealing at 600–700 °C; as the surface coverage of K increased, the surface transformed from 4×4 to 2×2 and finally to 1×1 relative to the original (111) surface (Shaikhutdinov et al. 1999). LEED and low energy ion scattering (LEIS) indicated that the $\sqrt{2} \times \sqrt{2}$ R45 surface of the magnetite (100) plane is due to ordering of vacancies among the tetrahedral Fe atoms in the surface layer (Mijiritski et al. 2000).

LEED, reflection high energy diffraction (RHEED) and AES together showed that an FeO film on an MgO substrate is unstable at room temperature, at even low exposure to oxygen (5.10^{-6} mbar) and transforms to magnetite (Ruby et al. 1999). LEED showed that the (100) surface of a crystal of natural goethite is well ordered and stable under the beam and has a long range order consistent with that of the bulk structure (Rakovan et al. 1999).

7.9

Microscopy

The surfaces of large Fe oxide crystals are commonly examined by various forms of optical microscopy. One such method, *phase-contrast* microscopy which involves a shift in the phase of the different light rays, can image surface features less than one nanometre in height. It has been used to show the spiral growth steps on the (001) plane of crystals of natural hematite (Sunagawa & Benema, 1979). *Differential interference contrast* microscopy (DIC) can detect similar height differences. This technique uses a Wollaston prism to split the light rays from an image and an analyser to create interference between them. The interference colours vary for the surface regions with different orientations and so enhance the contrast between them. DIC microscopy has been used to image the growth features on a sample of natural goethite (Rakovan et al. 1999).

Owing to their small particle size, submicron Fe oxides are routinely examined by transmission (TEM) and scanning electron microscopy (SEM). SEM has a large depth of field and a huge magnification range. It provides a 3D image and information about morphology and microtopography, whereas TEM usually provides a 2D image and is applied to very small crystals. Variants of TEM, viz. dark field microscopy and high resolution transmission electron microscopy (HRTEM) provide additional structural information and are used to follow phase transformations (e.g. Giovanoli & Brüttsch, 1975; Watari et al., 1979, 1979 a). Details of all these techniques and their applications are given in Bowen & Hall (1975) and Fryer (1979). An elec-

tron interference technique involving TEM, *electron holography*, has provided an estimate of the thickness of spindle-shaped hematite crystals (Shindo et al. 1998).

Two relatively new techniques with great potential to image small particles on the atomic scale are *scanning tunnelling microscopy* (STM) and *atomic* or *scanning force microscopy* (AFM or SFM) (Hochella et al., 1989; Maurice, 1998). STM involves measurement of a tunnelling current flowing between a sharp metallic tip and a surface a few tenths of a nm distant. The current is very sensitive to the distance between the tip and the sample and as the tip moves over the sample surface it follows the microtopology and produces a 3D image. In AFM on the other hand, a sharp tip mounted on a cantilever is moved across the sample surface and the deflections of the tip as it moves are monitored and translated to produce a 3D image of the surface. The AFM can operate either in the repulsive mode (the tip touches the surface and is repelled by it) or attractive mode (the tip is deflected towards the surface by Van der Waals forces). Both STM and AFM can be operated under vacuum, in air or under water, thus providing the possibility of *in situ* examination of specimens and crystal growth/dissolution. Both techniques can provide resolution on the atomic scale. They differ in that STM is limited to conducting and semiconducting surfaces, whereas AFM applies to insulators as well.

STM has been used to image the microtopography and the atomic structure of hematite (001) (Eggleston et al., 1990, Condon et al. 1995; Becker et al. 1996; Fischer et al. 1996; Shackhutinov & Weiss, 1999). Atomic STM images of this surface may depend on whether imaging was carried out under vacuum, in air or in an oil medium. Some authors report that both an Fe and an O₃ terminated surface coexist on (001) (Wang et al. 1998), whereas Eggleston (1999) presents arguments for only Fe contributing to the tunneling current. STM has been used to examine Cr^{III} adsorbed on hematite (Eggleston & Stumm, 1993). STM has also been used to examine the (001) plane of magnetite (Wiesendanger et al. 1992); atomic resolution was achieved together with selective imaging of the octahedrally coordinated Fe(B) sites and, with a ferrimagnetic tip, the different magnetic ions, Fe²⁺ and Fe³⁺. Subsequently, the (110) and (111) planes have been imaged (Tarrach et al. 1993; Jansen et al. 1995; Gaines et al. 1997; Seioche et al. 1999, Mijiritskii et al. 2000). The hematite (001) face has been imaged in both air and water (Johnssen, et al. 1991) using AFM. This technique has revealed fine, topographical details, not visible with TEM, on the surface of goethite crystals (Weidler et al. 1996; Fischer et al. 1996; see Plate IV.1). Weidler et al. (1998) used SFM to follow the *in situ* growth of the (001) and (101) faces of goethite and measured the growth rates and Barron et al. (1997) examined goethite grown epitaxially on hematite. AFM can also be used to provide information about surface charge characteristics with force-distance measurements: as yet, the data obtained is rather imprecise, although reasonable estimates of the pzc of hematite have been obtained (see chap. 10). Multiple-energy X-ray holography was used to image the atomic structure of hematite (Gog et al. 1996).

7.10

Thermoanalysis

The commonly used methods for thermoanalysis of Fe oxides are thermal gravimetric (TGA) and differential thermal analysis (DTA) and, occasionally, differential scanning calorimetry (DSC) (Mackenzie, 1957, 1981; Smykatz-Kloss, 1974). *Gravimetric thermograms* provide information about the temperature-dependent weight loss of an oxide. To obtain these, the sample is continuously heated at a constant rate ($2\text{--}10\text{ }^{\circ}\text{C min}^{-1}$) and its weight is measured using a balance. Fe-oxides containing structural OH, for example, goethite and lepidocrocite, lose weight at between $250\text{--}400\text{ }^{\circ}\text{C}$ by the dehydroxylation reaction: $2\text{ OH}^{-} \rightarrow \text{O}^{2-} + \text{H}_2\text{O}$. Even pure oxides such as hematite contain some OH in the structure, if fine-grained, but this is driven off over a much wider temperature range than is that of the FeOOH forms. Fine-grained material normally contains an appreciable amount of adsorbed water which leads to a weight loss between $100\text{ and }200\text{ }^{\circ}\text{C}$ and this can usually be distinguished from water of dehydroxylation. Additional weight loss occurs with schwertmannite through loss of SO_4^{2-} as SO_3 (Fig. 7.18; left).

Differential thermoanalysis involves recording the temperature difference between an inert compound and the sample during heating. Such differences occur if reactions take place which either release (exothermic effect) or consume (endothermic effect) energy. These effects are recorded as peaks on a plot of the temperature difference versus the temperature. Such thermal effects are associated with the loss of adsorbed H_2O and structural OH as in TGA and also with phase transformations.

Figure 7.18 (left) shows typical differential thermograms of Fe oxides. The first endotherm at $100\text{--}200\text{ }^{\circ}\text{C}$ is due to the release of adsorbed water, the amount of which depends on the particle size and the pretreatment of the sample. For the FeOOH forms it is followed by a second endotherm due to dehydroxylation. For both synthetic and natural *goethites* the temperature of this second endotherm increases with increasing crystal size, crystal order and Al-for-Fe substitution. For example, as the synthesis temperature increased from $4\text{ to }80\text{ }^{\circ}\text{C}$, goethite crystallinity improved and the endothermic peak temperature shifted from $260\text{ to }320\text{ }^{\circ}\text{C}$ (Schwertmann, 1984). In addition, a double peak developed, which in well-crystalline goethites is attributed to a two-phase transition to hematite (see Chap. 14). Increasing Al-for-Fe substitution also leads to higher peak temperatures for dehydroxylation and to a splitting of the dehydroxylation endotherm (Fig. 7.18, middle) (Schulze & Schwertmann, 1984).

With *lepidocrocite* the dehydroxylation endotherm due to transformation to maghemite is followed by an exotherm indicating transformation of maghemite to hematite. The temperature of the dehydroxylation endotherm was found to increase from $270\text{ to }300\text{ }^{\circ}\text{C}$ as Al substitution rose from Al/(Fe+Al) of 0 to 0.12 (Schwertmann & Wolska, 1990) and that of the exotherm rose from $500\text{ to }650\text{ }^{\circ}\text{C}$ (Wolska et al., 1992). Synthetic *feroxyhyte* shows a weak dehydroxylation endotherm at ca. $260\text{ }^{\circ}\text{C}$ (Carlson & Schwertmann, 1980).

In the thermogram of *akaganéite* Paterson et al. (1982) found adsorbed water was lost at ca. $100\text{ }^{\circ}\text{C}$, giving rise to a double dehydroxylation endotherm between 250

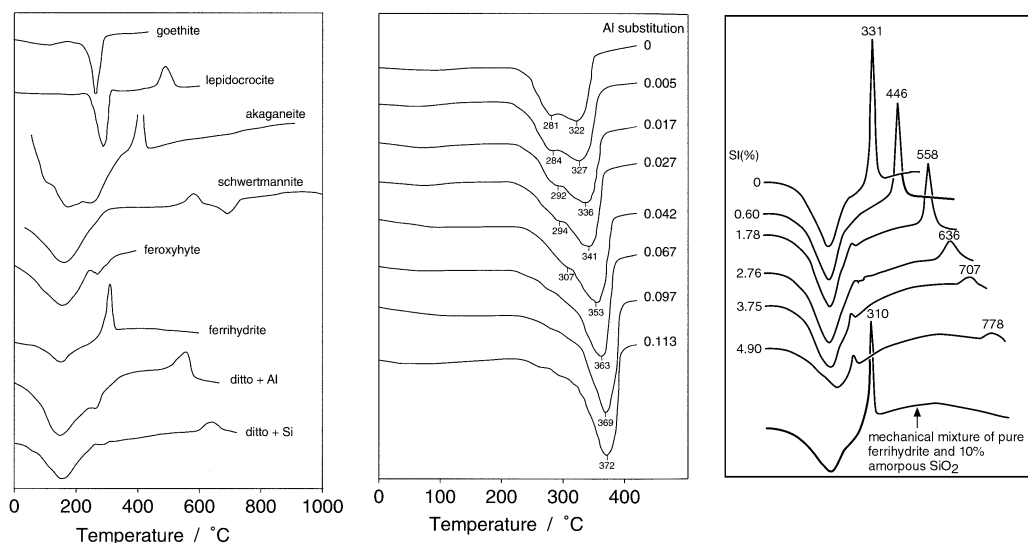


Fig. 7.18 Left: Differential thermograms (DTA curves) of different Fe^{III} oxides. (Carlson & Schwertmann, 1981 and unpubl.; with permission). Middle: DTA curves of goethites with increasing Al-for-Fe substitution Al/(Fe + Al) (Schulze & Schwertmann, 1984; with permis-

sion). Right: Effect of Si on the DTA curves of 2-line ferrihydrite; The numbers on the exothermic peak indicate temperature. The lowest thermogram is for a mechanical mixture of ferrihydrite and 10% amorphous SiO₂ (Carlson & Schwertmann, 1981; with permission)

and 300 °C which they assigned to the dehydroxylation of different surface OH (see Chap. 10). The other feature is a sharp exotherm whose temperature depends on the purge gas (N₂, O₂) and which is attributed to the release of Cl, an essential constituent of akaganeite. As in ferrihydrite, however, this peak may also be connected with the recrystallization of hematite. *Schwertmannite* shows in addition to an endotherm at low temperature, an exo-/endotherm pair at around 600 °C which can be attributed to the formation of Fe₂(SO₄)₃ followed by its decomposition to hematite and SO₃. This is also connected with a weight loss (Fig. 7.18) Dehydroxylation of the FeOOH part of the structure probably merges with the adsorbed water loss at low temperature because of the poor crystallinity of the sample.

Owing to its higher water content the low-temperature endotherm of *ferrihydrite* is strong. Ferrihydrite does not show a dehydroxylation peak. There is, however, a sharp exotherm when ferrihydrite turns into hematite. The presence of both Al and Si (Carlson & Schwertmann, 1981; Campbell et al. 2002) in ferrihydrite weakens and broadens this exotherm and shifts it to higher temperatures (Fig. 7.18; right). The mechanical mixture (lowest thermogram) has no effect and this indicates that in the coprecipitate Si and Fe are associated which hinders the transformation to hematite. *Bernalite* exhibits a strong exotherm between 190 and 200 °C at which temperature it is converted to hematite (Birch et al., 1993). Thermograms of *magnetite* show two exotherms corresponding to transformation first to maghemite and then to hematite. These exotherms approach each other as the particle size (< 300 to > 550 nm) in-

creases (Egger & Feitknecht, 1962). The temperature of the 2nd exotherm increased from 600 to 800 °C with increasing Al substitution (Wolska, 1990).

7.11

Dissolution Methods

Iron oxides can usually be dissolved in strong mineral acids or reductants. In mixtures with other minerals, as in rocks and soils, reductants are preferred because they are remarkably selective for Fe oxides although Mn oxides are also dissolved. Na₂S₂O₄, sodium dithionite, is the favoured reductant of soil scientists (see Chap. 12 and 16) (Mehra & Jackson, 1960). In most cases the entire Fe oxide component can be readily dissolved overnight at RT, or within hours at elevated temperatures (80 °C). Difficulties arise when the surface is not fully accessible due to cementation, a common phenomenon in natural oxides, but this can be overcome by pregrinding the sample. Strong mineral acids are normally used for pure synthetic Fe oxides. As an alternative to Na₂S₂O₄, Na₂SO₃, H₂S, Na₂S and H₂, the latter produced by reaction of Zn metal with an acid, have been used. Extraction by microbiological reduction has been suggested for soils to simulate the process by which Fe oxides are reduced in anaerobic soils, but the complete reduction usually takes about 2 weeks (Allison & Scarseth, 1942; Bromfield & Williams, 1963).

A second dissolution method used frequently for natural materials and synthesis studies is a 2 h extraction with 0.2 M oxalate, pH 3.0 (Tamm, 1922, 1933). If light, i.e. photochemical reduction is excluded, oxalate tends to separate ferrihydrite and schwertmannite from the better crystalline oxides goethite, hematite etc. reasonably well (Schwertmann, 1959, 1964; MacKeague & Day, 1966). The separation is better, the larger the difference in dissolution rate between these oxides. Thus, the separation is very suitable and has often been used for following the transformation of 2-line ferrihydrite to goethite/hematite. Since the rate of dissolution is a function of surface area (see Chap. 12), increasing proportions of better crystallized oxides dissolve as their surface area increases (Schwertmann, 1973). This may lead to slight dissolution in oxalate of very small (<10 nm) goethite crystals, especially after prolonged treatment; small crystals also have greater solubility. Lepidocrocite is more prone to dissolve than goethite of the same surface area. Akaganéite has a very high solubility in oxalate buffer (Kauffman & Hazel, 1975).

Some methods for differential dissolution of Fe-phases in sediments are suggested in chapter 15.

8

Thermodynamics of the Fe-O₂-H₂O system

8.1

General

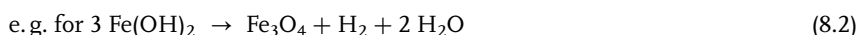
It is often necessary to predict which Fe oxide will form under a particular set of conditions and whether a single compound or a mixture can be expected (see chap. 13 and 14). This information is important for planning laboratory and industrial syntheses and for understanding how certain Fe oxides occur in nature. Much of the basic information in this field has been obtained by geoscientists (cf. Krauskopf, 1982).

A clear guide as to which compound is thermodynamically feasible under any set of conditions is obtained from the change in free energy, ΔG , for the reaction under consideration. The free energy or chemical potential is the driving force of the reaction and decreases until the system is at equilibrium. As the natural tendency is to minimize the chemical potential, a reaction only goes in the direction of the products if the free energy change is negative, i.e. energy is released and the products are stable with respect to the reactants. At equilibrium, the free energy change is zero. For many chemical reactions, the position of equilibrium is so far to the right that for all practical purposes, the reaction can be regarded as having gone to completion.

To calculate the total free energy change of a reaction, ΔG_r , it is necessary to know the standard molar free energy of formation, ΔG_f^0 , of each component involved, i.e. the energy required to form one mole of a substance from its stable elements under standard conditions. For a solid, the standard state refers to a pure substance in its most stable form under reference conditions of pressure and temperature, usually 0.1 MPa and 25 °C (298.15 K).

The standard free energy change that accompanies a chemical reaction is the difference between the sum of the free energies of formation of the products minus the sum of those of the reactants, i.e.

$$\Delta G_r^0 = \Delta G_{f, \text{prods}}^0 - \Delta G_{f, \text{reacts}}^0 \quad (8.1)$$



$$\Delta G_r^0 = (-1015.1) + (0) + 2(-238.2) - 3(-486) = -33.8 \text{ kJ mol}^{-1} \quad (8.3)$$

indicating that at 25 °C and 0.1 MPa pressure, Fe(OH)₂ is thermodynamically unstable and will eventually decompose to magnetite, water and hydrogen gas. Note that the free energies depend on the coefficient in the reaction and also that the free energy of an element (H₂) is zero. As $\Delta G_r^0 = \Delta H^0 - T\Delta S^0$, the standard free energy of an isothermal reaction, can be calculated from the standard free enthalpy, ΔH^0 (heat of reaction) and the standard free entropy, ΔS^0 . The standard free enthalpy of an element in its standard state is zero. Table 8.1 lists the ΔG^0 , ΔH^0 and ΔS^0 values for the iron oxides and Table 8.2 those for the soluble Fe species, together with those for a number of other compounds or elements involved in and therefore needed for, calculating free energy changes for reactions involving formation of iron oxides.

8.2

Standard free energy of reaction and the equilibrium constant

The standard free energy change of a reaction can be related to its equilibrium constant. For the reaction,



the reaction quotient can be formulated, viz.

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (8.5)$$

for which either concentrations [] or activities () may be used. The activity is the effective concentration of a substance in solution. It refers to the system in the standard state. Only in infinitely dilute solutions are activities and concentrations equal. The ratio of the activity of an ion species *i*, *a_i*, to its concentration, *c_i*, is called the activity coefficient, *γ_i*, i.e.

$$\gamma_i = a_i / c_i \quad (8.6)$$

The activity coefficient enables corrections for the non-ideality of a system to be made. It decreases as ionic strength increases. In infinitely dilute solutions, *a_i* = *c_i*, i.e. *γ_i* = 1.

The relationship between the total free energy of the reaction and the reaction quotient is given by (*R* = universal gas constant; *T* = absolute temperature);

$$\Delta G_r = \Delta G_r^0 + RT \ln Q \quad (8.7)$$

At equilibrium, $\Delta G_r = 0$ and the reaction quotient *Q* becomes the thermodynamic equilibrium constant, *K*. Hence, at equilibrium,

$$\Delta G_r^0 = -RT \ln K \quad (8.8)$$

Tab. 8.1 Standard free energies, enthalpies and entropies of formation of the iron oxides at 0.1 MPa and 298 K

<i>Solid</i>	ΔH_f° <i>kJ mol⁻¹</i>	ΔS_f° <i>kJ mol⁻¹ K⁻¹</i>	ΔG_f° <i>kJ mol⁻¹</i>	<i>Source</i>
Goethite	-559.3	60.5	-488.6	1
			-488.8	2
			-482.9	3
			-492.1	4
Lepidocrocite	-562.9	60.38 ⁰	-477.7	5
			-554.6-	11
			-556.4	12 ^{&}
Akaganéite	-557.6	62.5	-486.3	6
			-752.7	11
Ferrihydrite			-699	3
			(-712)	
Fe(OH) ₂	-569	87.9	-486	7
			-568.8	8
			79.59	3
Hematite	-824.6	87.4	-484.2	3
			492	
			-742.7	1
			-741.8	8
Magnetite	-823.13	90.06	-746.2	9
			-828.2	87.7
			-744.3	10, 16
			-826.2	87.4
h-Magnetite	-1115.7	146.1	-1012.6	1, 10
			-1015.1	8
			-1016.1	9
Maghemite	-	-	-945.79	17
Maghemite _{tetr.}	-812.7	-	-711.14	3
Maghemite _{cubic}	-805.8	87.4	-	11
			-723.9	13 ^{&}
FeO	-812.3	91.4	-	11
			-725.1	13 ^{&}
Wüstite	-272	59.8	-251	1
			-243.5	18
Green Rust*-SO ₄	-	-	-244.6	8
			-251.74	9
Ditto	-	-	-3795 ± 15	14
Green Rust**+Cl	-	-	-3669 ± 4	15
Green Rust*+-CO ₃	-	-	-2146 ± 5	14
	-	-	-3590 ± 10	14

1) Robie et al., 1978; 2) Berner, 1969; 3) Langmuir, 1969, 1971; 4) Diakonov et al., 1994; 5) Van Schuylenborgh, 1973; 6) Calc. by Murray, 1979; 7) Wagman et al., 1982; 8) Garrels & Christ, 1965; 9) Helgeson, 1969; 10) Hemingway, 1990. 11) Laberty & Navrotsky, 1998; 12) Diakonov, 1998; 13) Diakonov 1998 a; 14) Refait et al. 1999; 15) Hansen et al. 1994; 16) O'Neill, 1988; 17) Stolen & Gronvold, (1996); 18) Haavik et al. (2000)

* Fe^{II} Fe^{III} (OH)₁₂SO₄; ** Fe^{II} Fe^{III} (OH)₈Cl; + Fe^{II} Fe^{III} (OH)₁₂CO₃; § computed from Lindsay (1979)

0 natural sample; & calculated

Tab. 8.2 Standard free energies, enthalpies and entropies for soluble Fe and some other species (25 °C)

<i>Species</i>	ΔH^0 <i>kJ mol⁻¹</i>	ΔS^0 <i>kJ mol⁻¹ K⁻¹</i>	ΔG^0 <i>kJ mol⁻¹</i>	<i>Source</i>
Fe ³⁺	-49.6	-277	-17.2	6
	-47.75	-293	-10.55	2
			-16.83	3
Fe ²⁺	-89.1	-138	-78.8	2
FeOH ²⁺	-324	-29.2	-229.4	2
			-240.2	4
Fe(OH) ₂ ⁺	-	-	-438	2
Fe ₂ (OH) ₂ ⁴⁺	-	-	-467.3	2
Fe(OH) ₄ ⁻	-1050	74	-845	5
			-814.6	1
FeOH ⁺	-	-	-277.3	2
H ₂ O _l			-238.2	2
OH ⁻	-230	-10.75	-157.5	2
H ⁺			0	
H ₂	0	130.6	0	2
O ₂ g	0	205	0	2
O ₂ aq.	-11.7	111	16.32	2
			27.3	
Fe	0	27.3	0	2

1) Langmuir, 1969; 2) Wagman et al., 1982; 3) Garrels & Christ, 1965; 4) Baes & Messmer, 1976; 5) Diakonov et al. 1999; 6) Shock & Helgeson, 1988.

This relationship enables ΔG_r^0 for a reaction to be calculated from the experimentally determined equilibrium constant. Alternatively, if K is difficult to measure experimentally (as, for example, in the case of certain solubility products) the same expression may be used to obtain K from ΔG^0 .

The equilibrium constant depends on the temperature at which a reaction takes place, but at any given temperature, it is independent of pressure. If the standard enthalpies of the reactants and products of a reaction are known, the equilibrium constant for the reaction at a temperature other than that of the standard state may be calculated using the van't Hoff equation, i. e.

$$\frac{d(\ln K)}{dT} = \frac{(\Delta H_{\text{prods}}^0 - \Delta H_{\text{reacts}}^0)}{RT^2} \quad (8.9)$$

T is the temperature of the reaction. The linear form of the equation is,

$$\ln \frac{K_T}{K_{T^0}} = \frac{(\Delta H_{\text{prods}}^0 - \Delta H_{\text{reacts}}^0)}{R} \left(\frac{1}{T^0} - \frac{1}{T} \right) \quad (8.10)$$

Tab. 8.3 Heat capacity function coefficients for iron oxides

Oxide	<i>a</i>	<i>b</i>	<i>c</i>	Temperature range (K)	Reference
Goethite	100.671	$-0.83486 \cdot 10^{-2}$	$-0.21199 \cdot 10^7$	298–500	Diakonov et al. 1994
Lepidocrocite	62.205	0.067665	$-0.81564 \cdot 10^6$	298–500	Diakonov, 1998
Maghemite _{tetr}	87.5	0.7518		295–700	Diakonov, 1998a
Maghemite _{cub}	52.94	0.1713		298–600	Diakonov, 1998a
Magnetite: $C_p = 2659.108 - 2.52153T + 1.36769 \cdot 10^{-3} T^2 - 3.645541 \cdot 10^4 T^{-0.5} + 2.07344 \cdot 10^7 T^{-2}$				(290–800K)	(Hemingway, 1990)
Hematite: $C_p = -200.43 - 0.5601T + 1.4464 \cdot 10^{-4} T^2 + 20.680T^{0.5} + 0.6649 \cdot 10^4 T^{-1}$				(288–950K)	(Robie et al. 1979)

T^0 is the temperature of the standard state. This approximation usually holds over a narrow range of temperatures where ΔH can be assumed to be independent of temperature. Where ΔH is dependent on temperature, it can be evaluated from a knowledge of the heat capacity, C_p , i. e.

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta C_p(T) dt \quad (8.11)$$

$\Delta C_p(T)$ is the difference between the heat capacities of the products and the reactants at temperature, T . The heat capacity, C_p , is the rate of change of enthalpy with temperature at constant pressure. The dependence of C_p on T is given by,

$$C_p = a + bT + cT^{-2} + \dots \quad (8.12)$$

where a , b , c etc. are constants. At 298.15 °C, the standard heat capacity, C_p ($J \text{ mol}^{-1} \text{ °C}^{-1}$), for the different Fe oxides is: goethite 74.33 (Diakonov et al. 1994); lepidocrocite 76.2 (Diakonov, 1998); hematite 103.85 (Hemmingway, 1990); maghemite (tetr.) 110.3; maghemite (cubic) 104.0 (Diakonov, 1998a); magnetite 150.31 ± 0.8 ; wüstite: 49.98 ± 0.4 (Samsonov, 1982). Values of the constants are listed in Table 8.3.

The enthalpy of a reaction can be obtained experimentally with the aid of the van't Hoff equation by measuring the equilibrium constant, K , over a range of temperatures and plotting $\ln K$ against $1/T^2$ to give a straight line the slope of which is $\Delta H^0/R$.

8.3

Redox reactions

Iron has two common valence states, 2+ and 3+, hence oxidation-reduction (redox) reactions in the $\text{Fe-O}_2\text{-H}_2\text{O}$ system must be taken into account. A redox reaction involves transfer of electrons between reacting species. Such a reaction can be divided into two half cell reactions, one describing gain of electrons and the other, their loss. For example, the reduction of Fe^{3+} to Fe^{2+} by hydrogen gas,



can be broken up into two half cell reactions, i. e.



E^0 is the standard redox potential in Volts. By convention, the half cell reactions are always written as reduction reactions.

The overall free energy of the redox reaction can be calculated using the standard free energies for the half reactions. As ΔG^0 for the hydrogen half cell is zero and ΔG^0 for the electrons cancels out,

$$\Delta G_r^0 = \Delta G_{\text{Fe}^{2+}}^0 - \Delta G_{\text{Fe}^{3+}}^0 = -74.29 \text{ kJ mol}^{-1} \quad (8.16)$$

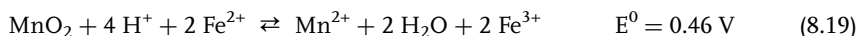
The two half reactions of any redox reaction together make up an electrochemical cell. This cell has a standard potential difference, E^0 , which is the voltage of the reaction at 25 °C when all substances involved are at unit activity. E refers to the potential difference when the substances are not in the standard state. E^0 for a particular reaction can be found by subtracting one half cell reaction from the other and also subtracting the corresponding voltages. For example for reduction of Fe^{3+} to Fe^{2+} by H_2 , $E^0 = 0.77 - 0 = 0.77 \text{ V}$. A further example is the oxidation of Fe^{2+} by solid MnO_2 in acid solution. The half cell reactions are,



and



In this case the first equation is subtracted from the second and also multiplied by 2 to balance the electrons. The voltages are also subtracted, but not multiplied (unlike free energies) because the potential difference does not depend on the amount of substance involved. Hence, the overall equation is,



For the overall reaction to occur spontaneously, the electrode potential must be positive. For eq. (8.19)

$$\Delta G_r^0 = -2 \cdot 96.5 \cdot 0.46 = -88.87 \text{ kJ mol}^{-1} \quad (8.20)$$

As electrochemical energy is simply another form of free energy, it can be related to the free energy of the reaction ΔG_r^0 , by the following relationship,

$$\Delta G_r^0 = -nFE^0 \quad (8.21)$$

where n is the number of electrons involved in the reaction and F is a constant termed the Faraday ($F = 96500$ coulombs).

From eq. (8.8) and (8.20), it follows that E^0 is also related to the equilibrium constant of the reaction, i.e.

$$E^0 = -\frac{RT}{nF} \ln K \quad (8.22)$$

For any reaction occurring under conditions other than standard ones, the Nernst equation for the redox potential E (often written as E_h) is used:

$$E = E^0 - \frac{RT}{nF} \log Q = E^0 + \frac{0.059}{n} \log Q \quad (8.23)$$

For the oxidation of Fe^{2+} by MnO_2 (eq. 8.19) the Nernst equation is:

$$E = 0.46 - \frac{0.059}{2} \log \frac{a_{\text{Mn}^{2+}} \cdot a_{\text{Fe}^{3+}}^2}{a_{\text{H}^+}^4 \cdot a_{\text{Fe}^{2+}}^2} \quad (8.24)$$

For oxidation at pH 5 and with unit activities for solid MnO_2 and the cations one obtains:

$$E = 0.46 - 0.03 \log \frac{1}{(10^{-5})^4} = 0.14 \quad (8.25)$$

Eq. (8.25) indicates that as the pH is raised, oxidation becomes less favourable. The Nernst equation can also be used to predict which species will predominate in a solution at a particular redox potential. For the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple ($E^0 = 0.77$ V), for example, in an aqueous solution with $E_h = 0.2$ V, we have

$$0.2 \text{ V} = 0.77 - 0.059 \log \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} \quad (8.26)$$

and $a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}$ will be $10^{9.32}$. At an E_h of 0.2V, which corresponds to less oxidizing conditions, the predominant species is Fe^{2+} .

Non-redox equilibria are expressed in terms of equilibrium constants based on activities, whereas E_h is given in volts. To compare and combine redox equilibria with other non-redox equilibria it is often convenient to use another term, p_e . p_e is the negative logarithm of electron activity based on the hydrogen half cell in which the redox activity is set at unity. Because p_e is expressed as mol L^{-1} , this term enables redox equilibria and other equilibria to be combined and expressed in terms of a single constant.

Take, for example, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. The redox potential in the $\text{Fe-O}_2\text{-H}_2\text{O}$ system controls the ratio of Fe^{2+} to Fe^{3+} according to the reaction,



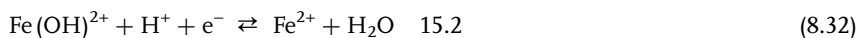
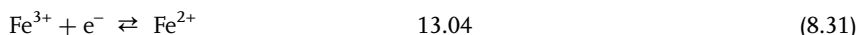
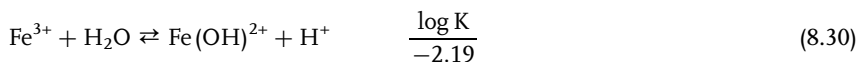
hence

$$\log \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} - \log e = \log K \quad (8.28)$$

and when the activities of the ions are equal to unity,

$$-\log e = \text{pe} = 13.04 \quad (8.29)$$

The reduction of Fe³⁺ can now be combined with the hydrolysis of Fe³⁺ to Fe(OH)²⁺, i. e.



$$K = \frac{a_{\text{Fe}^{2+}}}{e^- \cdot a_{\text{H}^+}^3 \cdot a_{\text{Fe}(\text{OH})^{2+}}} \text{ and again when the activities of the Fe species are unity,}$$

this reduces to;

$$\text{pe} = 15.2 - \text{pH} \quad (8.33)$$

8.4

Effect of complexing agents on redox potential

Both Fe²⁺ and Fe³⁺ can form complexes with species other than water or OH⁻. Complexation can cause marked changes in the electrode potential of the two oxidation states. The difference in standard single potentials between the hydrated and the complexed ions is given by,

$$E_{\text{compl}}^0 - E_{\text{hydr}}^0 = \frac{-(\Delta G_{\text{compl}}^0 - \Delta G_{\text{hydr}}^0)}{nF} \quad (8.34)$$

and can be calculated from the stability constants for the appropriate complexation reactions.

The standard electrode potentials, E⁰ (V) for some chelates of the Fe²⁺/Fe³⁺ redox couple are as follows: o-phenanthroline, 1.20; 2,2'-bipyridyl 1.096; water, 0.77; cyanide, 0.10; oxalate, -0.01 and 8-hydroquinone, -0.15 (Latimer, 1952). In the case of bipyridyl

and o-phenanthroline, chelation increases the stability of Fe^{2+} and the electrode potential of the couple is more positive than that in the aqueous system. On the other hand, for ligands such as oxalate, chelation increases the stability of both oxidation states, but to a greater extent for Fe^{3+} owing to its higher charge. Hence the electrode potential for the oxalate/ Fe^{2+} / Fe^{3+} couple is more negative than that for the aqueous system.

8.5

Stabilities of iron oxides

8.5.1

“Bulk” crystals

The standard free energy data listed in Tables 8.1 and 8.2 can be used to calculate the relative stabilities of the different iron oxides. The stability domains of these compounds are commonly plotted as functions of two variables, the most important of which are pH, Eh, temperature, pressure and pO_2 . A stability diagram provides a guide to what compound *may* form under any particular conditions, but because, particularly under ambient conditions, the kinetics of transformations of Fe oxides are often sluggish, metastable phases are frequently observed and may exist over long periods of time. Full details of how to construct such diagrams are given by Garrels and Christ (1965). Relevant stability constants and equilibria for pH/Eh diagrams are listed in Tables 8.1; 8.2; 8.4; 9.2 and 9.4.

Stability diagrams frequently involve the hematite/magnetite pair. The variables used depend upon whether the oxidation of magnetite to hematite is written in terms of O_2 or water. In a temperature/pressure diagram, hematite is the most stable phase at 640K and at a pO_2 of 10^{-23} mbar, whereas at pO_2 of 1 bar, the stability extends up to 1690K. For aqueous systems, the stability diagram is usually an Eh/pH diagram and magnetite predominates in alkaline media under reducing conditions, whereas hematite is stable over an extremely wide pH range under oxidizing conditions. However, depending on the data used, the hematite domain can equally well be occupied by goethite or by metastable phases such as maghemite or the other FeOOH polymorphs. In other words, the results of the calculations may not be in accord with what is actually observed. There are two reasons for this: metastable phases can exist for long periods of time and, the thermodynamic data available may not apply to the existing phases. Furthermore, as the stability of an oxide may depend on particle size, surface energy must be taken into account.

There is a lot of thermodynamic data for goethite, hematite, magnetite and wüstite, but far less for maghemite and the other polymorphs of FeOOH . Diakonov and his coworkers have critically evaluated the experimental data from the literature and used it to construct a self consistent set of surface and bulk thermodynamic properties at 298K for goethite (Diakonov, 1998a), lepidocrocite (Diakonov, 1998) and maghemite (Diakonov, 1998a)¹⁾. The experimental data included heats of solution, high

1) The data is fully discussed in Diakonov's papers.

Tab. 8.4 List of reactions for dissolved species in Fe-H₂O systems and corresponding pH dependence of *E* (Misawa, 1973; with permission)

<i>Reactions</i>	<i>Equilibrium formula</i>
$\text{H}_2 = 2 \text{H}^+ + 2 \text{e}^-$	$E = 0.000 - 0.0592\text{pH} - 0.0296 \log P_{\text{H}_2}$
$2 \text{H}_2\text{O} = \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$	$E = 1.229 - 0.0592\text{pH} + 0.0148 \log P_{\text{O}_2}$
$\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^-$	$E = 0.771 + 0.0592 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$
$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+ + \text{e}^-$	$E = 0.916 - 0.0592\text{pH} + 0.0592 \log \frac{[\text{FeOH}^{2+}]}{[\text{Fe}^{2+}]}$
$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + 2 \text{H}^+ + \text{e}^-$	$E = 1.194 - 0.1183\text{pH} + 0.0592 \log \frac{[\text{Fe}(\text{OH})_2^+]}{[\text{Fe}^{2+}]}$
$\text{FeOH}^+ + \text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + \text{H}^+ + \text{e}^-$	$E = 0.796 - 0.0592\text{pH} + 0.0592 \log \frac{[\text{Fe}(\text{OH})_2^+]}{[\text{FeOH}^+]}$
$\text{FeOH}^+ + 3 \text{OH}^- = \text{Fe}(\text{OH})_4^- + \text{e}^-$	$E = 1.781 - 0.1775\text{pH} + 0.0592 \log \frac{[\text{Fe}(\text{OH})_4^-]}{[\text{FeOH}^+]}$
$\text{Fe}(\text{OH})_3 + \text{OH}^- = \text{Fe}(\text{OH})_4^- + \text{e}^-$	$E = 0.381 - 0.0592\text{pH} + 0.0592 \log \frac{[\text{Fe}(\text{OH})_4^-]}{[\text{Fe}(\text{OH})_3]}$
$\text{Fe}(\text{OH})_4^- = \text{Fe}(\text{OH})_4^{2-} + \text{e}^-$	$E = -0.477 + 0.0592 \log \frac{[\text{Fe}(\text{OH})_4^-]}{[\text{Fe}(\text{OH})_4^{2-}]}$
$\text{Fe}^{3+} + 4 \text{H}_2\text{O} = \text{FeO}_4^{2-} + 8 \text{H}^+ + 3 \text{e}^-$	$E = 2.197 - 0.1578\text{pH} + 0.0197 \log \frac{[\text{FeO}_4^{2-}]}{[\text{Fe}^{3+}]}$
$\text{FeOH}^{2+} + 3 \text{H}_2\text{O} = \text{FeO}_4^{2-} + 7 \text{H}^+ + 3 \text{e}^-$	$E = 2.154 - 0.1380\text{pH} + 0.0197 \log \frac{[\text{FeO}_4^{2-}]}{[\text{FeOH}^{2+}]}$
$\text{Fe}(\text{OH})_2^+ + 2 \text{H}_2\text{O} = \text{FeO}_4^{2-} + 6 \text{H}^+ + 3 \text{e}^-$	$E = 2.053 - 0.1183\text{pH} + 0.0197 \log \frac{[\text{FeO}_4^{2-}]}{[\text{Fe}(\text{OH})_2^+]}$
$\text{Fe}(\text{OH})_4^- = \text{FeO}_4^{2-} + 4 \text{H}^+ + 3 \text{e}^-$	$E = 1.735 - 0.0789\text{pH} + 0.0197 \log \frac{[\text{FeO}_4^{2-}]}{[\text{Fe}(\text{OH})_4^-]}$

temperature heat capacity measurements and the high temperature enthalpies of dehydration reactions. In some cases, application of the data was hampered by uncertainties regarding the surface area of the solids used by earlier workers.

For lepidocrocite, the calculated value of $\Delta H_f^0 = -556.4 \pm 2 \text{ kJ mol}^{-1}$, is the average of the enthalpies calculated using the experimental values of different authors. In all cases, the surface areas of the samples were estimated using information provided about the size of the crystals; corrections for the surface enthalpies are, therefore, uncertain. However, this calculated average accords quite well with the recently measured value of $-554.5 \text{ kJ mol}^{-1}$ of Laberty and Navrotsky (1998). Diakonov (1998a) also provided a set of self consistent data for both the tetragonal and cubic forms of maghemite but points out that this is a first approximation because, in view of the scatter in entropy data ($S_f^0 = 71\text{--}117 \text{ kJ mol}^{-1}\text{K}^{-1}$), the S_f^0 of hematite was used and, furthermore, there was no reliable low temperature solubility data against which to check ΔG_f^0 . Diakonov's calculated ΔH_f^0 is somewhat higher than the experimental value obtained by Laberty and Navrotsky (1998) (Tab. 8.1).

The only available value of ΔG_f^0 for akaganéite was calculated by Murray (1979) using the solubility data of Biedermann and Chow (1966) and appears to be too low. The measured value for ΔH_f^0 (Laberty & Navrotsky, 1998) is comparable with that of the other oxide hydroxides. No data for $\delta\text{-FeOOH}$ is available as yet.

These comments indicate that for some iron oxides, reliable free energy values are not available, hence calculations based on existing data may provide no more than an estimate of the most stable compound of a pair. For the *goethite/hematite* pair, reasonably accurate values exist, but the difference between them is small and may be influenced by factors such as particle size. Prediction of the ΔG_f^0 of the most stable member of the pair is, therefore, difficult. A statement of R.M. Garrels may, in this context, be of general significance: "If one assemblage of phases differ from another by a free energy change of ca. 8 kJ mol^{-1} or less, either assemblage may form or exist." The following discussion is, therefore, limited to fairly clear cases in which the predictions of relative stabilities also agree with observations from laboratory experiments and/or natural environments.

Transformations which are thermodynamically feasible and can be induced under laboratory conditions, are often not observed in nature. For example, probably as a result of sluggish kinetics, the transformation of *lepidocrocite* into goethite has neither been observed under ambient conditions in the laboratory, nor in soils on a pedogenic time scale (see Chap. 16). The transformation of lepidocrocite to hematite or maghemite is only possible at high temperatures. The same applies to *akaganéite* the transformation of which in nature, to the more stable goethite has not been observed. The maghemite $\rightarrow$ hematite conversion is another that has only been observed in the laboratory. Values of ΔH_f^0 (285K) for this transformation were calculated by Diakonov (1998a) from literature data and range from $-15.6 \pm 3.5 \text{ kJ mol}^{-1}$ (Ferrier's data, 1966) to $-25.3 \pm 0.6 \text{ kJ mol}^{-1}$ (Derwent & Zerweck's data, 1937). The experimental value of $-14.1 \pm 1.5 \text{ kJ mol}^{-1}$ for commercial (100 % pure) maghemite is close to the lower end of the calculated values (Laberty & Navrotsky, 1998). The latter authors reported an enthalpy of oxidation of magnetite to hematite of $-119.6 \text{ kJ mol}^{-1}$. The fact that the thermodynamically unstable 2-line *ferrihydrite* is the initial product of the rapid hydrolysis of Fe^{III} solutions is an illustration of the Ostwald law of stages, i.e. when a solid can exist as both a crystalline and a poorly ordered (or amorphous) phase, the less ordered, more soluble phase is the first precipitated. It might be expected that as goethite is less soluble (see Tab. 9.4), it should form first. Precipitation of the poorly ordered phase occurs, however, if the interfacial free energy of its critical nucleus is sufficiently below that of the crystalline phase to offset the higher supersaturation. Preferential precipitation of ferrihydrite also suggests that the stable critical nucleus of ferrihydrite is smaller than the unit cell dimensions of goethite and hence the less ordered atomic arrangement of ferrihydrite may be energetically the more favourable one.

$\text{Fe}(\text{OH})_2$ is thermodynamically unstable with respect to magnetite (eq. (8.2) and (8.3)) and other Fe^{III} compounds. It can, however, exist as a metastable phase for limited periods. *Wüstite*, FeO , is only stable at temperatures greater than 570°C . At lower temperatures it disproportionates to Fe^0 and Fe_3O_4 . Figure 8.1 shows the stability domains for wüstite, iron and magnetite as a function of temperature and oxygen content. The phase boundaries of wüstite at high pressures have been estab-

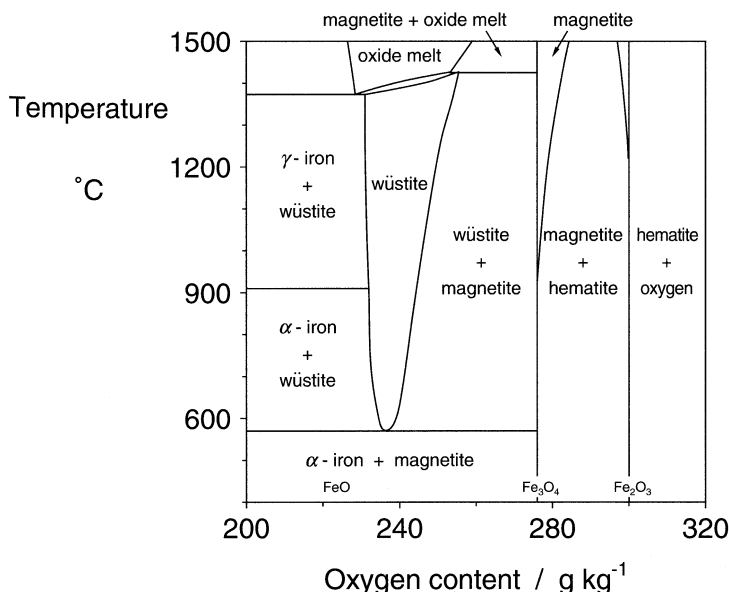


Fig. 8.1 Phase diagram of the Fe-O system (Bogdandy & Engell, 1971; with permission).

lished by Stølen & Grønvold (1996) and the thermodynamics of the FeO system at high pressure, investigated by Haavik et al. (2000).

Both the thermodynamic data and the experimental evidence indicate that two of the most stable Fe^{III} oxide phases are *goethite* and *hematite*. There has been considerable controversy over which of these phases is the more stable. Under ambient conditions, as for example, in surface environments, goethite appears to be more stable than hematite. This observation, however, only applies to the rather rare, massive crystals. From a consideration of all available data concerning heats of dissolution, Diakonov et al. (1994) derived a “best” value for the standard enthalpy of formation of goethite, $\Delta H_{f(298)}^0$ of -562.9 ± 1.5 kJ mol⁻¹ and a standard Gibbs free energy of formation, $\Delta G_{f(298)}^0$ of -492.1 ± 1.5 kJ mol⁻¹. From the data of Ferrier (1966), they also calculated “best” values for the standard enthalpy of the dehydroxylation reaction of goethite to hematite in the presence of liquid and gaseous water as $\Delta H_{r(298)}^0 = 13.6 \pm 3.5$ kJ mol⁻¹ and 57.1 ± 3.5 kJ mol⁻¹, respectively.

Figure 8.2 depicts the stability fields of goethite and hematite as a function of temperature and water pressure using data from several sources. The graph shows clearly that as the temperature increases, the stability field for hematite widens (see also Chap. 14). The goethite stability field broadens as P_{H_2O} increases. At $P_{H_2O} = 0$, the equilibrium temperature is 100 °C and rises to 300 °C at $P_{H_2O} = 2$ MPa.

Robins (1967) plotted the stability domains of these two oxides as a function of temperature, pH and [Fe^{III}]. Hematite predominated over the pH range 0–3 at temperatures above 150–200 °C; the stability field of hematite widened as [Fe^{III}] increased.

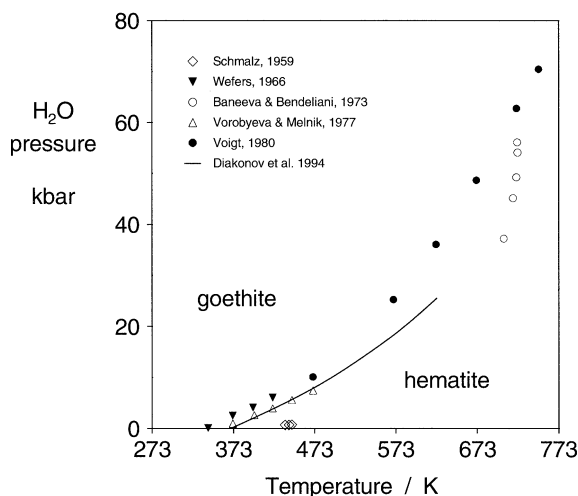


Fig. 8.2 Stability fields of goethite and hematite as a function of temperature and H_2O pressure (Diakonov et al., 1994; with permission).

So far the discussion of the goethite/hematite equilibrium refers to aqueous systems in which the *water activity* (i.e. relative humidity), $a_{\text{H}_2\text{O}}$, is unity. In many cases, however, the water activity may be < 1 . This applies to soils and sediments where $a_{\text{H}_2\text{O}}$ can be lowered by the binding of water in pores. When considering the dehydroxylation reaction,



Tardy and Nahon (1985), therefore, introduced $a_{\text{H}_2\text{O}}$ as a variable. When both oxides are in equilibrium, the value of this variable is given by,

$$\log a_{\text{H}_2\text{O}} = 2 \log *K_{\text{so,Gt}} - \log *K_{\text{so,Hm}} \quad (8.36)$$

and, therefore, depends on the values chosen for K_{so} (see Chap. 9).

Trolard and Tardy (1987) calculated an equilibrium water activity of ca. 0.6 at 5°C , 0.78 at 15°C , 0.88 at 25°C and 0.9 at 40°C . At higher temperatures, hematite should be the stable phase even at an $a_{\text{H}_2\text{O}}$ of unity. Experimental confirmation of the importance of the relative humidity on the direction of the reaction is provided by the work of Torrent et al. (1982). This study also demonstrated that at $a_{\text{H}_2\text{O}} < 1$, the transformation of *ferrihydrite* into more stable phases is very slow.

8.5.2

Effect of particle size and Al substitution

As discussed further in Chapter 9, energy relationships are also influenced by surface properties, which must be taken into account once the crystals become smaller than ca. $1\ \mu\text{m}$ (Tab. 8.5). Langmuir (1971) calculated $\Delta G_{\text{r}(298)}^0$ in liquid water as a function of particle size, using differential heat of solution values (as a function of

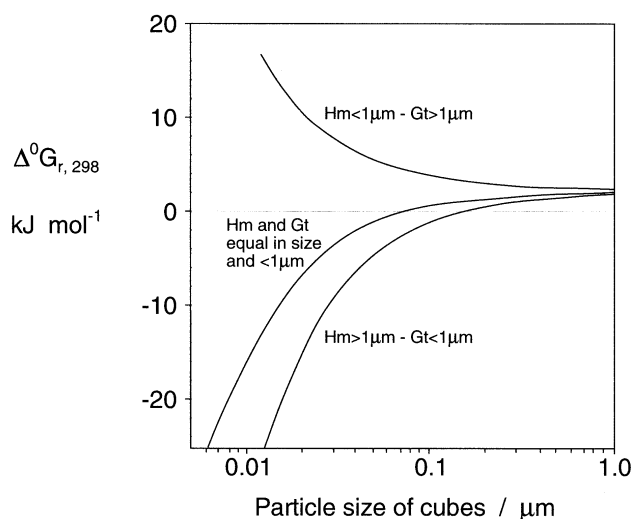
Tab. 8.5 Apparent surface thermodynamic properties for goethite and hematite at 298.15K (see Diakonov et al. 1994)

Solid	$H \text{ [Jm}^{-2}\text{]}$	$S \text{ [mJm}^{-2}\text{K}^{-1}\text{]}$	$G \text{ [Jm}^{-2}\text{]}$
Goethite	1.55	0.5	1.400
Hematite	1.100	0.5	0.950

oxide surface area) and third law entropy measurements. He derived the relationship (d = crystal dimension in μm),

$$\Delta G_{r(298)}^0 (\text{kJ mol}^{-1}) = 2.28 \pm 2.51 - \frac{0.342}{d_{\text{Gt}}} + \frac{0.163}{d_{\text{Hm}}} \quad (8.37)$$

Naturally, this result will depend on the value used for ΔG_f^0 of the bulk (massive) oxide (Tab. 8.1). Plots of $\Delta G_{r(298)}$ as a function of particle size are shown in Figure 8.3. They suggest that when the goethite crystals are $> 1 \mu\text{m}$ and those of hematite are $< 1 \mu\text{m}$, hematite should transform to goethite. If crystals of both oxides are of equal size, hematite is less stable above and goethite less stable below a particle size of around $0.08 \mu\text{m}$. Finally, if hematite is $> 1 \mu\text{m}$ and goethite $< 1 \mu\text{m}$, goethite is the more stable down to a particle size of ca. $0.15 \mu\text{m}$. These predictions about the stabilities of the two oxides do not, however, agree with experimental *in situ* observations. Regardless of the crystal sizes, the transformation of goethite to hematite under ambient conditions has not been observed, nor has the reverse transformation.

**Fig. 8.3** Particle size effect on the Gibbs free energy of the reaction $2 \text{ goethite (Gt)} \rightarrow \text{hematite (Hm)} + \text{H}_2\text{O}$ at 25°C (Langmuir, 1971; with permission).

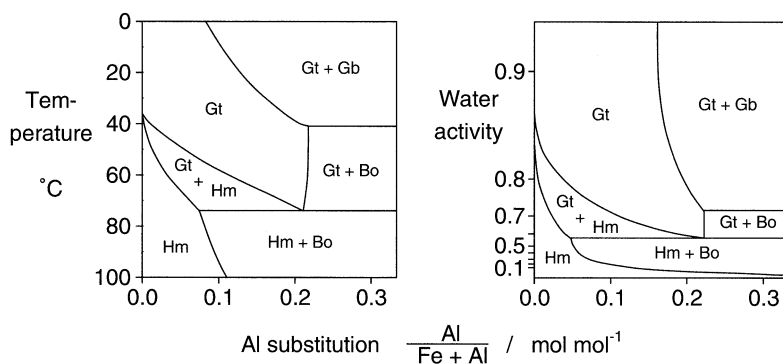


Fig. 8.4 Stability fields of Al-goethite and Al-hematite as a function of Al substitution.

Left: at various temperatures and constant water activity of 1.0.

Right: at various water activities and a constant temperature of 25 °C (Trolard & Tardy, 1987; with permission).

Langmuir's approach, therefore, appears to require further development before it can be used as a predictive tool. Long term experiments to test whether this transformation occurs have not been carried out.

Using a calculated solubility product $\log K_{so}$ for well crystallized (bulk) goethite of -42.4 ± 0.4 and recalculated values (from data of earlier workers) of surface free energy of $1400 \pm 200 \text{ mJ m}^{-2}$ for goethite and $950 \pm 200 \text{ mJ m}^{-2}$ for hematite, Diakonov et al. (1994) concluded that coarse grained goethite is stable relative to hematite up to a temperature of 40 °C. At 25 °C, goethite should be stable relative to coarse grained hematite down to a particle size of 150 nm, a situation which often occurs in natural systems. Experimental studies to determine the equilibrium solubility of fine grained goethite and hematite at 85 °C in liquid water showed that goethite was unstable with respect to hematite (Berner, 1969) in agreement with the above.

Tardy and Nahon (1985) and Trolard and Tardy (1987) considered the effect of Al for Fe substitution on the stability of goethite and hematite in the temperature range 5–80 °C and a_{H_2O} range 0–1 at a total pressure of 0.1 MPa. It was assumed that there was an ideal solid solution between the respective end members goethite/diaspore and hematite/corundum (Fig. 8.4). In order to obtain agreement with observations made in natural systems, they used a new set of $\log K_{so}$ values for the various oxides. The general result was that increasing the Al/Fe mole ratio in the systems narrowed the stability field of Al-hematite and widened that of Al-goethite. This again, however, is not in agreement with what has been observed during formation of the oxides from ferrihydrite in laboratory syntheses where Al in the system strongly favoured hematite over goethite, hence a kinetic explanation is preferred (Schwertmann et al. 2000) (see Chap. 14).

9

Solubility

9.1

General

The solubility of solid is determined by the free energy of dissolution, i.e. the difference between the lattice energy of the solid and the hydration energy of its ions. Where the lattice energy is much greater than the hydration energy, the solubility of the solid is low.

In general, the solubility of Fe^{III} oxides is low and Fe^{II} oxides are sparingly soluble. This means that except at extreme pH values, these compounds maintain a very low level of total Fe (Fe_T) in solution. In the pH range 4–10 and in the absence of complexing or reducing agents Fe_T is $< 10^{-6} \text{ M}$. Iron oxides dissolve slowly over a wide pH range. The similarity of both the kinetic and thermodynamic behaviour is, however, fortuitous; there is no general relationship between the rate at which a solid dissolves and its solubility.

9.2

The solubility product

The extent to which a sparingly soluble solid dissolves is expressed by the solubility product. This describes the equilibrium established between the solid and the concentration of its ions in a saturated solution. Consider, for example, the dissolution of goethite in water:



To characterize the solution composition, activities, a_i , instead of concentrations have to be used (see Chap. 8). At equilibrium the following expression can be formulated:

$$\frac{a_{\text{Fe}^{3+}} \cdot a_{\text{OH}^-}^3}{a_{\text{FeOOH}} \cdot a_{\text{H}_2\text{O}}} = K \quad (9.2)$$

At a given temperature, K is constant and as a_{FeOOH} and the concentration of water are also constant, the three can be combined to give

$$a_{\text{Fe}^{3+}} \cdot a_{\text{OH}^-}^3 = K_{\text{so}} \quad (9.3)$$

K_{so} is the solubility product. It applies to iron oxides, hydroxides and oxide hydroxides.

An alternative representation of the solubility product which is useful in acid media, is in terms of an equilibrium reaction between the oxide and protons,



The solubility product is:

$$a_{\text{Fe}^{3+}} \cdot a_{\text{H}^+}^{-3} = {}^*K_{\text{so}} \quad (9.5)$$

or

$$\log a_{\text{Fe}^{3+}} = \log {}^*K_{\text{so}} - 3\text{pH} \quad (9.6)$$

From eq. (9.6) the activity of Fe^{3+} in equilibrium with the solid phase can be calculated as a function of pH; this relationship is linear and has a slope of -3 .

K_{so} can be obtained from ${}^*K_{\text{so}}$ by replacing a_{H^+} by $K_{\text{w}}/a_{\text{OH}^-}$ (K_{w} = ion product of water) as shown in the following example involving hematite in a low ionic strength solution at 25 °C:

	log K	
$\frac{1}{2}(\alpha\text{-Fe}_2\text{O}_3) + 3\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \frac{3}{2}\text{H}_2\text{O}$	-1.88	(9.7)
$3\text{H}_2\text{O} \rightleftharpoons 3\text{H}^+ + 3\text{OH}^-$	3 (-13.99)	(9.8)
$\frac{1}{2}(\alpha\text{-Fe}_2\text{O}_3) + \frac{3}{2}\text{H}_2\text{O} \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	-43.85	(9.9)

$$\frac{1}{2}(\alpha\text{-Fe}_2\text{O}_3) + \frac{3}{2}\text{H}_2\text{O} \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^- \quad (9.9)$$

$$\text{i. e. } {}^*K_{\text{so}} = K_{\text{so}}/K_{\text{w}}^3 \quad (9.10)$$

The ion product of water depends on the ionic strength of the system and on its temperature. At 25 °C and in low ionic strength solution, $\log K_{\text{w}} = -13.99$, whereas in 3 M NaClO_4 (the ionic medium used by Schindler et al., 1963 for solubility product determination), $\log K_{\text{w}} = -14.22 \pm 0.1$; the value chosen must correspond to the ionic strength of the system involved.

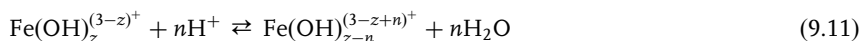
The comparison of the ion activity product (IAP) of the dissolved constituent ions (e.g. for goethite, Fe^{3+} and OH^-) with K_{so} of a Fe oxide provides an indication of whether the oxide will precipitate or dissolve in a particular solution. If the IAP exceeds K_{so} , the solution is supersaturated with respect to the oxide and precipitation takes place. If $\text{IAP} = K_{\text{so}}$, the system is in equilibrium and if $\text{IAP} < K_{\text{so}}$, the oxide will dissolve until equilibrium is reached. Interference with nucleation may retard or even inhibit precipitation in a supersaturated solution and prevent true equilibrium from being attained.

Dissolution to reach equilibrium from undersaturation may also be slow. Dissolution of magnetite at pH 4.5 in 0.1 M NaClO₄ (25 °C), reached equilibrium only after 20 days (Sun et al., 1998).

9.3

The effect of hydrolysis reactions and pH on solubility

The aquo-Fe³⁺ ion, [Fe(OH₂)₆]³⁺, is the predominant Fe^{III} species only at very low pH. As the pH rises above 1, Fe³⁺ hydrolyses in a stepwise manner to give a series of soluble, positive and (in alkaline media) negative hydroxo species (see Chap. 13). The different hydrolysis species raise the concentration of dissolved iron in equilibrium with the solid at any pH. The equilibrium between the solid oxide and its various hydroxo species in solution is represented by the equation:



Such equilibria and their stability constants are summarized in Table 9.1. The total concentration of dissolved iron (Fe_T) at any pH is given by the sum of the concentrations of the free metal iron and all the soluble hydrolysis species, i.e.

$$\text{Fe}_T = (\text{Fe}^{3+}) + (\text{FeOH}^{2+}) + (\text{Fe}(\text{OH})_2^+) + 2(\text{Fe}_2(\text{OH})_2^{4+}) + (\text{Fe}(\text{OH})_4^-) \quad (9.12)$$

$$= \text{Fe}^{3+} + \Sigma (\text{Fe}(\text{OH})_n^{(3-n)+}) \quad (9.13)$$

Tab. 9.1 Equilibria and experimentally determined stability constants for the iron hydroxo complexes (room temperature).

Equilibrium reaction	log K _{SM}	Reference
Fe(OH) ₂ + OH ⁻ → Fe(OH) ₃ ⁻	log K _{s3} = -4 (fresh) = -5.1 (aged)	1 ^{a)}
Fe(OH) ₂ + 2 OH ⁻ → Fe(OH) ₄ ²⁻	log K _{s4} = -4.5 (fresh) = -5.5 (aged)	1 ^{a)}
Fe(OH) ₃ + H ⁺ → Fe(OH) ₂ ⁺ + H ₂ O	log K _{s2} = 16.6 (fresh ppt) = 17.0 (aged)	1 ^{b)}
Fe(OH) ₃ + 2 H ⁺ → FeOH ²⁺ + 2 H ₂ O	log K _{s1} = -27.5 (fresh) = -27.9 (aged)	1 ^{b)}
Fe(OH) ₃ + OH ⁻ → Fe(OH) ₄ ⁻	log K _{s4} = -4.5 (fresh) = -4.9 (aged)	1 ^{b)}
2 Fe(OH) ₃ + 4 H ⁺ → Fe ₂ (OH) ₂ ⁴⁺ + 4 H ₂ O	log K _{s22} = -51.9 (fresh) = -52.7 (aged)	1 ^{b)}
α-FeOOH + H ₂ O → Fe(OH) ₃ ⁰	log K _{s3} = <-8.7	2 ^{b)}
α-FeOOH + H ₂ O + OH ⁻ → Fe(OH) ₄ ⁻	log K _{s4} = -6.2-7	2 ^{b)}
0.5 α-Fe ₂ O ₃ + 2.5 H ₂ O → Fe(OH) ₄ ⁻ + H ⁺	log K _{s4} = -21.9	3

1) Feitknecht and Schindler, 1963 (and references therein); 2) Lengweiler et al., 1961; 3) Diakonov et al., 1999. Background electrolyte a) 0 or dilute; b) 3M NaClO₄.

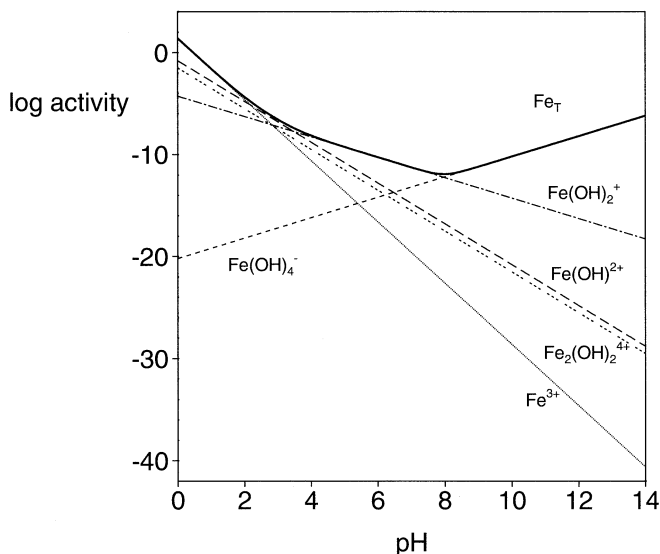


Fig. 9.1 Activities of single ion species and total Fe activity (Fe_T ; heavy line) in equilibrium with goethite as a function of pH.

The only known anionic species is $\text{Fe}(\text{OH})_4^-$.

The enhanced solubility that results from taking hydrolysis into account can be illustrated by plotting the logarithmic activities of the components of Fe_T as a function of pH. The resulting diagram shows at a glance differences between the solubilities of the different iron oxides. The solubility diagram for goethite is shown in Figure 9.1. The species to be considered are those of eq. (9.12). Their activities are found by combining the appropriate hydrolysis reaction constants (Tab. 9.1 and 9.2) with the solubility product (Tab. 9.4). For $\text{Fe}(\text{OH})_2^{2+}$, for example, the equations are,



Hence the relationship between FeOH^{2+} and pH is,

$$\log \text{FeOH}^{2+} = \log *K_{\text{so}} + \log *K_1 - 2 \text{ pH} \quad (9.17)$$

For the other hydrolysis species the dependence on pH is given by,

$$\log \text{Fe}(\text{OH})_2^+ = \log *K_{\text{so}} + \log *\beta - \text{pH} \quad (9.18)$$

$$\log \text{Fe}_2(\text{OH})_2^{4+} = 2 \log *K_{\text{so}} + \log *\beta_{22} - 4 \text{ pH} \quad (9.19)$$

Tab. 9.2 Hydrolysis equilibria and constants for the soluble Fe^{2+} and Fe^{3+} species at 25 °C (data from Baes and Mesmer, 1976).

Equilibrium reaction	log K
$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^+ + \text{H}^+$	-9.5
$\text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2^0 + 2 \text{H}^+$	-20.6
$\text{Fe}^{2+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3^- + 3 \text{H}^+$	-31.4
$\text{Fe}^{2+} + 4 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_4^{2-} + 4 \text{H}^+$	-46.4
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{2+} + \text{H}^+$	-2.19 (K_1)
$\text{Fe}^{3+} + 2 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2^+ + 2 \text{H}^+$	-5.67 (β)
$\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3^0 + 3 \text{H}^+$	<-12
$\text{Fe}^{3+} + 4 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_4^- + 4 \text{H}^+$	-21.6
$2 \text{Fe}^{3+} + 2 \text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{OH})_2^{4+} + 2 \text{H}^+$	-2.95 (β_{22})

$$\log \text{Fe}(\text{OH})_4^- = \log K_{s4} + \log \text{OH}^- \quad (9.20)$$

The sum of all the soluble Fe^{III} species, i.e. Fe_T , in equilibrium with goethite as a function of pH, is the heavy line in the solubility diagram in Figure 9.1, whereas the activities of the single species are shown by the weak lines. Inclusion of the hydrolysis species results in a much higher solubility than would be observed by consideration of the solubility product i.e. Fe^{3+} , alone. For example, at pH 6, $a_{\text{Fe}^{3+}}$ is $< 10^{-15}$ M, whereas $a_{\text{Fe}_T} = 10^{-11}$ M. Only at very low and very high pH is a_{Fe_T} essentially equal to $a_{\text{Fe}^{3+}}$ and $a_{\text{Fe}(\text{OH})_4^-}$, respectively.

The solubility plots for lepidocrocite, ferrihydrite and hematite (Fig. 9.2) and for goethite, ferrihydrite and “soil-Fe” (Fig. 9.3) show only the total Fe activity. They were obtained in the same way as that for goethite using the appropriate constants from Tables 9.1, 9.2 and 9.4.

The solubility diagrams indicate that for all the iron oxides under consideration, there is a region of minimum solubility around pH 7–8, i.e. around the point of zero charge (pzc) (see Chap. 10). As iron oxides are amphoteric, they dissolve in acid media to form cationic, hydroxo species and in basic media, to form anionic, hydroxo species. Hence, solubility rises as the pH moves away in either direction, from the pzc. There is considerable uncertainty about the solubility of iron oxides in the pH region 6–9. Although a neutral soluble species, $\text{Fe}(\text{OH})_3^0$, has been postulated by various authors, there is still uncertainty concerning its stability constant. Baes and Mesmer (1976) used the solubility data of Lengweiler et al., (1961) to estimate a $\log K_{s3} < -12$. In seawater, the value (at 25 °C) of $\log K_{s3}$ ranged from < -13.6 to -15 , depending upon the method used to measure soluble Fe^{III} (Kuma et al., 1992; Lui and Millero, 1999; Byrne et al., 2000). In view of all this, the neutral species is usually ignored in the construction of solubility diagrams and the plots calculated using the stability constants obtained in acidic and basic media are extrapolated to the region around pH 7.

Solubility diagrams have nearly always been *calculated* using solubility and stability constants. Experimental determination of the solubility of iron oxides as a function of pH has been concerned predominately with ferrihydrite. Lengweiler et al.

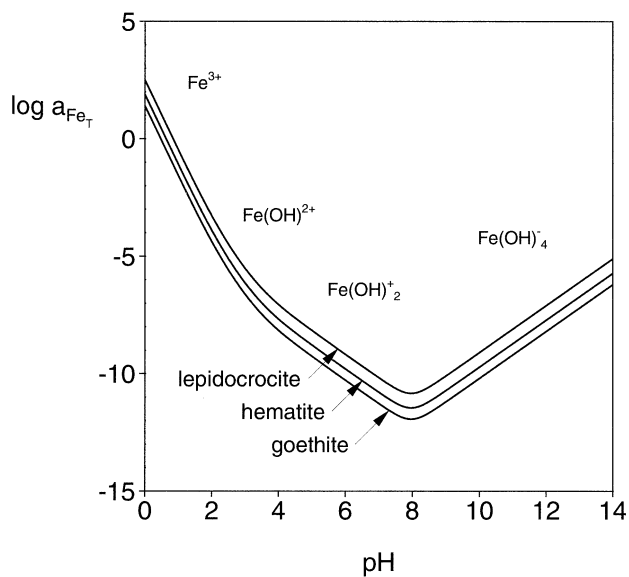


Fig. 9.2 Solubilities of goethite, hematite and lepidocrocite as a function of pH.

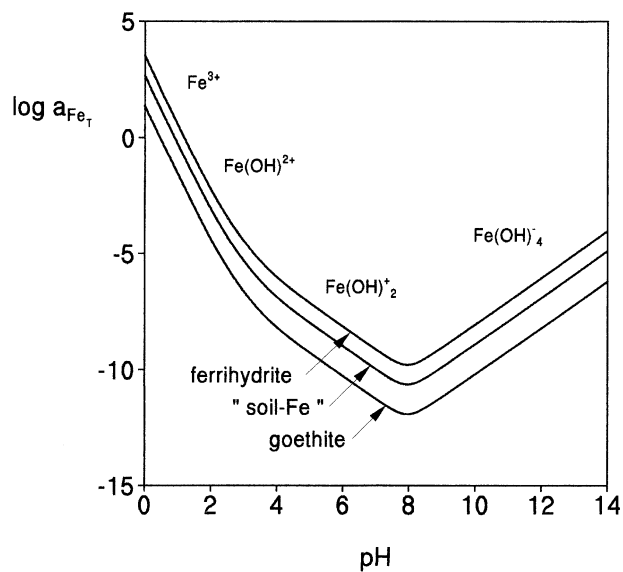


Fig. 9.3 Solubilities of goethite, ferrihydrite and "soil-Fe" as a function of pH (data for "Soil Fe" from Lindsay, 1979, with permission).

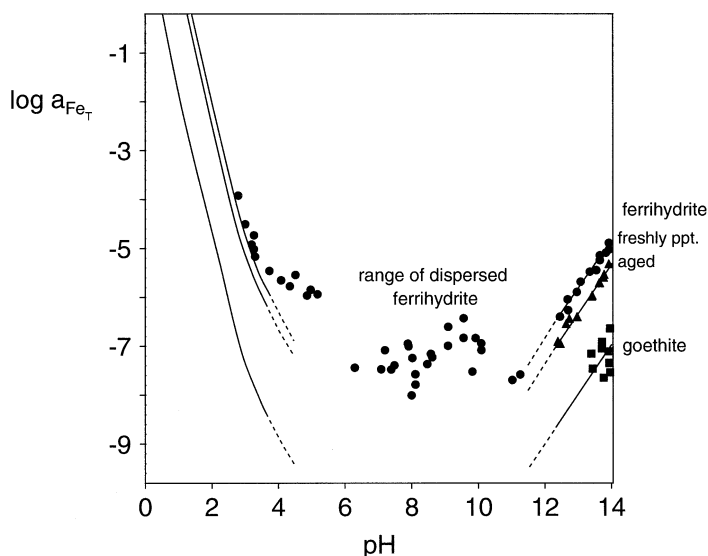


Fig. 9.4 Calculated and experimental solubility of ferrihydrite as a function of pH (Schindler et al., 1963, with permission). The curves were calculated taking into account the species Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_4^-$ and $\text{Fe}_2(\text{OH})_2^{4+}$ and the following solubility products: ($\log^*K_{so}$) ferrihydrite, freshly precipitated 3.96; ferrihydrite, aged 3.55 and goethite 1.4.

(1961) used a radiochemical method to measure the solubility of ferrihydrite up to pH 14. The experimental data agreed well with that calculated over the pH range 0–3.5 and 12.5–14. In the intermediate pH range, however, measured Fe_T (10^{-7} M) was some orders of magnitude greater than that calculated (Fig. 9.4). The authors used a centrifugation technique to show that the discrepancy was due to the presence of colloidal ferrihydrite ($d < 5$ nm), which passes through conventional filters, and is very difficult to separate from dissolved Fe. The presence of colloidal material can often be detected visually by the brownish tinge imparted to the solution.

Lengweiler et al. (1961) found that the solubility of goethite, like that of ferrihydrite, increased as the pH rose above 12. For ferrihydrite, equilibrium between the solid and $\text{Fe}(\text{OH})_4^-$ was reached quite rapidly, whereas for goethite, equilibrium was not reached even after 40 days (25 °C). A value of 1.40 ± 0.1 for $^*K_{so}$ of goethite (surface area ca. $100 \text{ m}^2\text{g}^{-1}$) was only reached after 3 years (Fig. 9.5) (Bigham et al., 1996). As expected on thermodynamic grounds, the solubility of goethite was 10^2 to 10^3 times less than that of ferrihydrite.

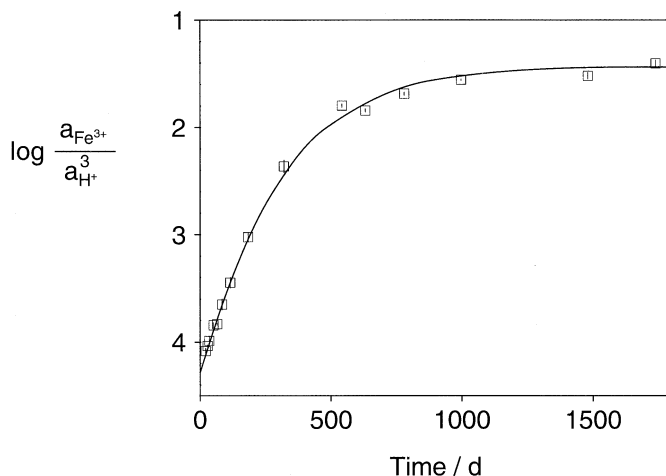


Fig. 9.5 Change of the activity ratio $a_{\text{Fe}^{3+}}/a_{\text{H}^+}^3$ with time during the transformation of schwertmannite to goethite (Bigham et al., 1996; with permission).

9.4

Other factors influencing solubility and the solubility product

The solubility and the hydrolysis constants enable the concentration of iron that will be in equilibrium with an iron oxide to be calculated. This value may be underestimated if solubility is enhanced by other processes such as complexation and reduction. Solubility is also influenced by ionic strength, temperature, particle size and by crystal defects in the oxide. In alkaline media, the solubility of Fe oxides increases with rising temperature, whereas in acidic media, the reverse occurs. Blesa et al., (1994) calculated $\log^*K_{\text{so}}$ values for Fe oxides over the temperature range 25–300 °C from the free energies of formation: for hematite, $\log^*K_{\text{so}}$ fell from 0.44 at 25 °C to –10.62 at 300 °C.

9.4.1

Complexation

The presence of ligands such as chloride, phosphate and citrate that form soluble complexes with Fe^{II} or Fe^{III} causes the *free* metal concentration in solution to decrease and thus enhances the solubility of the solid. In this case, for an Fe^{III} oxide, (L^- = ligand),

$$\text{Fe}_{\text{T}} = \Sigma \text{Fe}(\text{OH})_n^{(3-n)+} + \Sigma p\text{Fe}_p\text{L}_q^{(3p-q)+} \quad (9.21)$$



and

$$K_{so} = \frac{a_{\text{FeL}^{2+}} \cdot a_{\text{OH}^-}^3}{a_{\text{L}^-}} \quad (9.23)$$

For example the oxalate/ Fe^{III} system forms three complexes: FeOx^+ , $\text{Fe}(\text{Ox})_2^-$ and $\text{Fe}(\text{Ox})_3^{3-}$. These ligands markedly increase the solubility of Fe oxides. In a goethite/ 10^{-3} M oxalic acid system, the presence of the ligand increases $\log \text{Fe}_T$ from -5.3 (no ligand) to -3.0 at pH 2, from -7.5 to -3.4 at pH 3 and from -9.1 to -27.5 at pH 4. Above pH 5, however, the ligand has no effect because the hydroxyl ion competes successfully for sites in the coordination sphere of Fe. A large excess of complexing ligand over the Fe concentration may therefore hold Fe in solution or may shift its precipitation as an oxide towards a higher pH than in the absence of the ligand. Ferrihydrite precipitates from a 10^{-3} M Fe^{III} solution at pH 2–3; 10^{-2} M phosphate or citrate will, however, hold this amount of Fe^{III} as a soluble complex up to pH 4.8 and 7.6, respectively. These higher Fe concentrations are important for the supply of iron to plant roots which excrete organic ligands such as siderophores (see Chap. 16). In alkaline, sodium phosphate solution, the $\text{Fe}(\text{III})\text{-HPO}_4$ complexes appeared to control the solubility of magnetite (Ziemniak et al., 1995).

9.4.2

Redox reactions

Reducing conditions enhance the solubility of Fe^{III} oxides by promoting reductive dissolution, e. g.

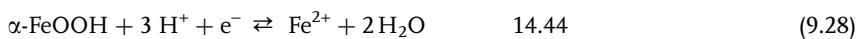


Dissolved Fe^{II} species contribute to Fe_T

$$\text{Fe}_T = \sum \text{Fe}(\text{OH})_n^{(3-n)+} + \sum \text{Fe}(\text{OH})_n^{(2-n)+} \quad (9.25)$$

A number of redox equilibria and their constants are listed in Table 9.3. Complexing agents can change these values (see Chap. 8).

The effect of reducing conditions on the solubility of an iron oxide can be found by combining the appropriate dissolution equations with the redox equation to obtain the concentration of the Fe^{II} species released. In the $\text{Fe}^{\text{II}}/\text{Fe}$ oxide system, protons are always involved because the state of hydrolysis of the Fe is changed. For goethite, for example,



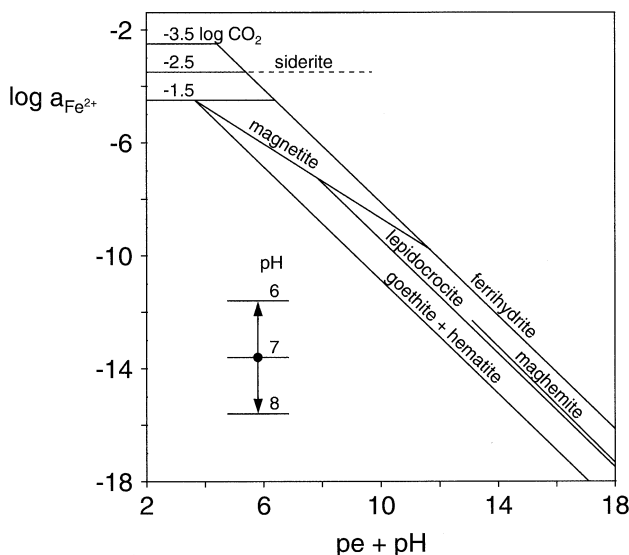
$$\text{hence } \log a_{\text{Fe}^{2+}} = 14.4 - \text{pe} - 3\text{pH} \quad (9.29)$$

$$= 14.4 - (\text{pe} + \text{pH}) - 2\text{pH} \quad (9.30)$$

Tab. 9.3 Redox equilibria and constants for the iron oxides (Lindsay, 1979).

Equilibria	log K
$\text{Fe}(\text{OH})_3 + 3 \text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 3 \text{H}_2\text{O}$	15.87
$\text{Fe}_3\text{O}_4 + 8 \text{H}^+ + 2 \text{e}^- \rightarrow 3 \text{Fe}^{2+} + 4 \text{H}_2\text{O}$	35.69
$\text{Fe}_3\text{O}_4 + 8 \text{H}^+ \rightarrow 3 \text{Fe}^{3+} + \text{e}^- + 4 \text{H}_2\text{O}$	-3.42
$\text{Fe}_{0.95}\text{O} + 0.1 \text{e}^- + 2 \text{H}^+ \rightarrow 0.95 \text{Fe}^{2+} + \text{H}_2\text{O}$	12.42

The use of $pe + pH$ to characterize a system is convenient, because this term separates the protons associated with the redox reaction from those associated with the effect of pH on the concentration of the reduced species. As $pe + pH$ falls, $a_{\text{Fe}^{2+}}$ in solution rises. Figure 9.6 shows the activity of Fe^{2+} in equilibrium with various Fe phases as a function of $pe + pH$ and also P_{CO_2} , at pH 7. The Fe^{2+} activity changes one hundred fold for each unit change in pH. Figure 9.7 compares the activity of Fe_T (a_{Fe_T}) released from goethite under oxidizing and reducing ($pe + pH = 8$) conditions. Reducing conditions enhance a_{Fe_T} (predominantly present as $\text{Fe}(\text{OH})^+$) over the acid/neutral pH range by up to four orders of magnitude. Using eq. (9.28) and the log K values of the different Fe^{III} oxides, Fischer (1985) calculated the Eh values (mV) necessary to produce an equilibrium Fe^{2+} activity in solution of 10^{-4} M at pH 7, to be 40 mV for ferrihydrite, -160 mV for lepidocrocite, -290 mV for hematite and -310 mV for goethite. This reflects the different stabilities of these oxides although the absolute values depend on the log K chosen.

**Fig. 9.6** The activity of Fe^{2+} in equilibrium with various Fe phases at pH 7, as a function of $pe + pH$ and P_{CO_2} (Lindsay, 1979; modified, with permission).

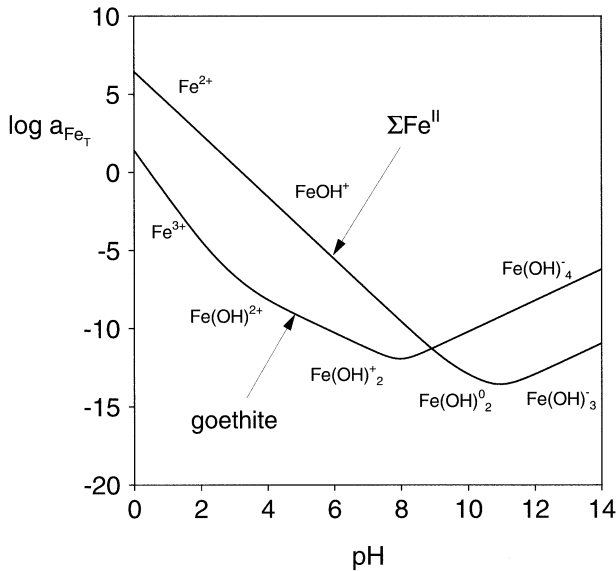


Fig. 9.7 The solubility of goethite under oxidizing and reducing conditions at $(pe + pH) = 8$.

9.4.3

Ionic strength

The solubility of a solid is a function of the ionic strength of the system. In dilute solutions, the solubility of a solid increases and K_{so} falls with rising ionic strength, owing to the increase in the interionic forces in solution. The data of Hsu and Marion (1985), combined with that of Schindler et al. (1963) show that as I increases from 0.005 to 3 M, $\log K_{so}$ of goethite decreases from -39.8 to -41.6 . In very concentrated solutions in which the activity coefficients exceed unity, the reverse trend may operate. Hence it is necessary to specify the ionic strength, I , at which the measurement of K_{so} was carried out. Stoichiometric solubility products which have been measured at some particular ionic strength can be corrected to conditions of zero ionic strength using the Debye-Hückel-equation or its extended form, to give the thermodynamic solubility product, $^T K_{so}$.

9.4.4

Properties of the solid

9.4.4.1 Particle size

The most important physical property of the solid that will affect solubility is particle size. For crystals $< 1 \mu\text{m}$, the high surface area may increase solubility. This occurs because it is the surface properties, especially the surface free energy, rather than the properties of the bulk solid, that govern the dissolution behaviour. Because the surface free energies of iron oxides are relatively high, particle size will have a marked

effect on the solubilities of the compounds. The relationship between the change in solubility associated with a change in particle size can be obtained by subdividing a bulk solid, suspended in water, into a finely divided material of molar surface area, A . The free energy, ΔG associated with this process is:

$$\Delta G = 0.66 \bar{\gamma} A \quad (9.31)$$

where $\bar{\gamma}$ is the mean free surface energy (interfacial tension) of the solid/liquid interface. As $\Delta G_T^0 = RT \ln K_{so}$, the solubility product (for a monodisperse system) can be related to the molar surface energy by the relationships,

$$\log K_{so(A)} = \log K_{so(A=0)} + \frac{0.66 \bar{\gamma} A}{2.3 RT} \quad (9.32)$$

or

$$\log K_{so(A)} = \log K_{so(A=0)} + \frac{0.66 \bar{\gamma} M \alpha}{2.3 RT d \sigma} \quad (9.33)$$

where $A = M\alpha/d$ and M is the molecular weight, σ the density of the solid (hence M/d = molar volume), α is a geometric shape factor and d is the particle size.

The change in the value of $\log K_{so}$ relative to that of the thermodynamically most stable form, as a result of the particle size effect, is then given as,

$$\delta \log K_{so} = \log K_{so(A)} - \log K_{so(A=0)} \quad (9.34)$$

$$\delta \log K_{so} = \frac{0.66 M \alpha \bar{\gamma}}{2.3 RT d \sigma} \quad (9.35)$$

Different authors have derived slightly different sets of equations relating K_{so} of goethite and hematite to the particle size of these oxides. Langmuir and Whittemore (1971) used the values of standard surface enthalpy ΔH_s , obtained by Ferrier (1966) viz. 1250 and 770 mJ m⁻² for goethite and hematite, respectively, and assuming the crystals to be cubes, related K_{so} to the cube edge length (nm), i. e.,

$$\log K_{so(Gt)} = \log K_{so(Bulk Gt)} + \frac{12.3}{d} \quad (9.36)$$

$$\log K_{so(Hm)} = \log K_{so(Bulk Hm)} + \frac{2.5}{d} \quad (9.37)$$

As seen from Figure 9.8 the calculated K_{so} increases by two orders of magnitude when the particle size decreases from 1 μ m to 10 nm, i. e. over the common range of hematite and goethite particle sizes in natural environments.

Using the ΔG_f^0 values of Robie et al. (1978) for goethite (-488.5 kJ mol⁻¹) and hematite (-742.68 kJ mol⁻¹) and Ferrier's ΔH_s values, Tardy and Nahon (1985) and Trolard and Tardy (1987) proposed similar equations involving $^*K_{so}$ instead of K_{so} , i. e.

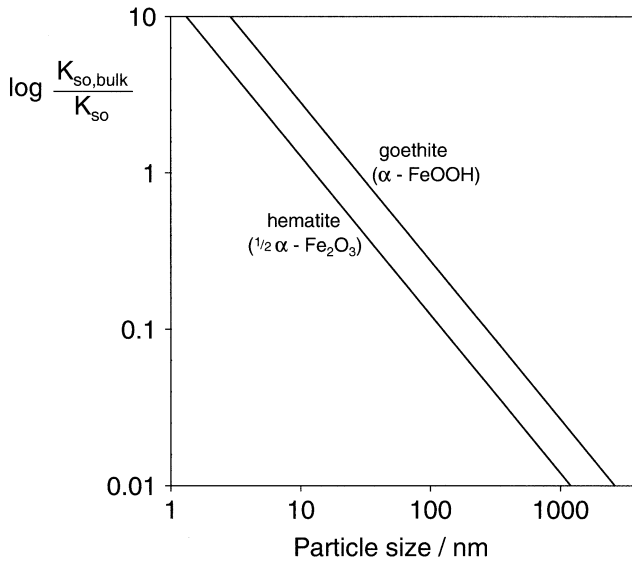


Fig. 9.8 Particle size effect on the solubility products of goethite and hematite (Langmuir and Whittemore, 1971, with permission).

$$\log *K_{so(Gt)} = -1.696 + \frac{27}{d} \quad (9.38)$$

$$\log *K_{so(Hm)} = -3.886 + \frac{25}{d} \quad (9.39)$$

In this case, d (nm) is the diameter of spherical particles. Both sets of equations are only approximations, particularly for goethite, the particles of which are often acicular. However, they do enable an estimate of the rise in solubility, as particle size drops, to be obtained (see Fig. 8.3). There is little difference between the results calculated using the two sets of equations for particles > 100 nm, but for 10 nm particles there is more than an order of magnitude difference between the two equations. The higher solubility of smaller particles may lead to their transformation to larger ones via solution, a process called *Ostwald ripening*.

Although the experimental data for ZnO and CuO has been shown to agree with the theoretical predictions (Schindler, 1967), the only known experimental investigation of the effect of particle size on K_{so} for iron oxides showed no definite correlation between the two parameters (Hsu and Marion, 1985). The samples had average lengths ranging from 700 (bulk) to 100 nm and a definite trend might have been observed, if even smaller particles had been investigated.

9.4.4.2 Ageing and isomorphous substitution

Other characteristics of the solid that influence its solubility are whether it has been freshly precipitated (formerly this material was termed “active”) or whether it has been aged (“inactive”) and also whether foreign ions are present in the structure. Ferrihydrite precipitates from highly supersaturated solutions as fine (2–5 nm) particles with a poorly ordered structure. With time, however, the solubility decreases (see Fig. 9.4).

Iron oxides can incorporate significant levels of different metal ions in the crystal structure – for example up to 0.15 and 0.30 mol mol⁻¹ Al in hematite and goethite, respectively (see Chap. 3). Calculations made assuming ideal solid solution behaviour for aluminous goethite and hematite suggest that the substituted oxides are the more stable (Fey, 1983; Trolard and Tardy, 1987) and their formation in preference to nonsubstituted forms is, therefore, predicted. Indeed, Al-substituted goethites are widespread in nature. No solubility products of substituted forms are yet available. It has been found, however, that substituted goethites and hematite dissolve more slowly in acids and in reducing solutions (see Chap. 12).

9.5

Methods of determining or calculating the solubility product

The equilibrium solubility of an Fe oxide can be approached from two directions – precipitation and dissolution. The first method involves precipitating the oxide from a supersaturated solution of ions with stepwise or continuous addition of base and using potentiometric measurements to monitor pH and calculate Fe_T in equilibrium with the solid phase until no further systematic change is detected. Alternatively the oxide is allowed to dissolve in an undersaturated solution, with simultaneous measurement of pH and Fe_T until equilibrium is reached. It is essential that neither a phase transformation nor recrystallization (formation of larger crystals) occurs during the experiment; this may happen with ferrihydrite which transforms (at room temperature) to a more condensed, less soluble phase. A discussion of the details of these methods is given by Feitknecht and Schindler (1963) and by Schindler (1963).

For iron oxides, long periods are often needed to reach equilibrium. Biedermann and Schindler (1957) found that an apparent steady state was reached for ferrihydrite via the precipitation method after 200 hours, but much longer time may be needed for less soluble oxides, such as goethite. During the transformation of metastable schwertmannite into stable goethite at 25 °C, it took several years before reasonably stable activities of Fe^{3+} , and H^+ were reached (Fig. 9.5). The resulting $\log^* K_{so}$ of 1.4 was in good agreement with the value found for goethite by Schindler et al. (1963). Errors arise as a result of the difficulty in establishing when equilibrium has been reached. The best test of the reliability of the measured solubility product for an iron oxide is whether the constants obtained by both the dissolution and precipitation methods are in agreement. Schindler et al. (1963) approached equilibrium via precipitation using a ferrihydrite that had been aged for one year at 25 °C in the pH range 1–2. They then carried out a dissolution experiment (some weeks) using ferrihydrite

that had been aged for 2 years. Both methods gave $\log *K_{\text{so}} = 3.55 \pm 0.1$ for ferrihydrite which can therefore, be regarded as a reliable value. Diakonov et al. (1999), obtained $\log K_{\text{S4}} = -19.64$ for hematite from both dissolution and precipitation experiments at 60°C .

Solubility products may be calculated using the free energies of formation of the oxide, the free metal ion, OH^- and water (Tab. 9.1 and 9.2). For goethite, for example,



$$\Delta G_{\text{f}} = \Delta G_{\text{f}_{\text{Fe}^{3+}}} + 3\Delta G_{\text{f}_{\text{OH}^-}} - \Delta G_{\text{f}_{\text{Gt}}} - \Delta G_{\text{f}_{\text{H}_2\text{O}}} \quad (9.40)$$

$$\Delta G_{\text{f}} = -10.59 + 3(-157.5) - (-488.8) - (-237.3) \quad (9.41)$$

$$\Delta G_{\text{f}} = 243.33 \text{ kJ mol}^{-1} = -5.706 \log K_{\text{so}} \quad (9.42)$$

$$\log K_{\text{so}} = -42.64 \quad (9.43)$$

The major problem with this method is that K_{so} depends very much on the free energy value of the iron oxides chosen. Values of $\log *K_{\text{so}}$ calculated for goethite and hematite using various free energies of formation taken from the literature range from -4.32 to 1.6 for goethite and from -2.16 to 0.85 for hematite (Trolard and Tardy, 1987). The calculated values are usually lower than the experimental values given in Table 9.4. A calculated value of $\log K_{\text{so}}$ of -42.4 ± 0.4 was obtained for goethite using a new ΔG_{f}^0 of $-492.1 \pm 1.5 \text{ kJ mol}^{-1}$ (Diakonov et al., 1994).

Tab. 9.4 Solubility products of the iron oxides at 25°C .

Oxide	Symbol for equilibrium constant	$\log K_{\text{so}}$ or $\log *K_{\text{so}}$	Reference
Goethite	* K_{so}	$1.4 \pm 0.8^{\text{a})}$	Schindler et al., 1963
	K_{so}	-40.7	Langmuir, 1969
	* K_{so}	$-0.02^{\text{b})}$	Lindsay, 1979
	* K_{so}	$0.82^{\text{b})}$	Tardy & Nahon, 1985
	K_{so}	$-39.80^{\text{c})}$	Hsu & Marion, 1985
	K_{so}	$-40.32^{\text{c})}$	" "
	K_{so}	$-40.83^{\text{c})}$	" "
	* K_{so}	1.40 ± 0.1	Bigham et al., 1995
	K_{so}	$-42.4 \pm 0.4^{\text{b})}$	Diakonov, 1998
	* K_{so}	2.72	Van Schuylenborgh, 1973
Lepidocrocite	* K_{so}	2.5	Hashimoto & Misawa, 1973
	K_{so}	-39.5	" "
	K_{so}	-42.48 ± 0.23	Vlek et al., 1974
	* K_{so}	1.39	Lindsay, 1979
	K_{so}	$-41.4^{\text{b})}$	Diakonov, 1998

Tab. 9.4 (continued)

Oxide	Symbol for equilibrium constant	$\log K_{so}$ or $\log^* K_{so}$	Reference
Akaganéite	* K_{so}	$3.04 \pm 0.05^d)$	Biedermann & Chow, 1966
Schwertmannite, nat	* K_{so}	17.4 ± 0.1	Bigham et al., 1995
Schwertmannite, syn	* K_{so}	$2.01 \pm 0.30^g)$	Yu et al., 2002
Ferrihydrite	* K_{so}	$3.96 \pm 0.1^a)$	Biedermann & Schindler, 1957
	* K_{so}	$3.55 \pm 0.1^a)$	Schindler et al., 1963
	K_{so}	-39.5	Langmuir & Whittemore, 1971
	K_{so}	-39.02 ± 0.35	Vlek et al., 1974
	* K_{so}	$4.3^g)$	Byrne & Kester, 1976
	K_{so}	$-31.7^f)$	Fox, 1988
	K_{so}	$-37.7^b)$	Diakonov, 1998
2-line Ferrihydrite	K_{so}	-4.23 ± 0.70	Yu et al., 2002
6-line Ferrihydrite	* K_{so}	-5.06 ± 0.37	" "
Fe(OH) ₂	* K_{so}	12.85 ± 0.2	Feitknecht & Schindler, 1963
	K_{so}	-15.15 ± 0.2	" "
	K_{so}	$-14^f)$	" "
Hematite	* K_{so}	$-1.88^b)$	Baes & Mesmer, 1976
	K_{so}	-42.75	" "
	* K_{so}	0.09	Lindsay, 1979
	* K_{so}	1.69	Tardy & Nahon, 1985
Magnetite	* K_{so}	$12.02^b)$	Sweeton & Baes, 1970
Maghemite	* K_{so}	1.59	Lindsay, 1979
	K_{so}	-40.41	" "
	K_{so}	$-40.5^b)$	Diakonov, 1998
	K_{so}	$-40.06 \pm 0.14^i)$	Sadiq & Lindsay, 1988
Soil-Fe ^{III} oxide	K_{so}	-39.0 ± 0.3	Bohn, 1967
	* K_{so}	2.7	Lindsay, 1979

a) Background electrolyte 3 M NaClO₄b) calculated from ΔG_f c) Ionic strength $5 \cdot 10^{-3}$, $4 \cdot 10^{-2}$; 0.2 M, resp.f) $(Fe^{3+})(OH^-)^{2.35}$ d) $(Fe^{3+})(H^+)^{-2.70}$

e) in sea water

f) freshly precipitated

g) for the reaction: $Fe_2O_{3-x}(SO_4)_x + (3+x)H_2O = 2Fe^{3+} + 6OH^- + xSO_4^{2-} + 2xH^+$

h) see Text

i) natural sample

9.6

Solubility products of the various oxides

Numerous measurements of the solubility products of ferrihydrite and goethite have been made (Table 9.4), but there are fewer for hematite, lepidocrocite, maghemite and magnetite and apparently none for FeO and δ -FeOOH. There are often discrepancies (of up to three orders of magnitude) between the results of different authors. As described above, some properties of the Fe oxides, especially particle size and crystallinity may explain some of these variations. Furthermore, some authors ignored hydrolysis species in their calculations, others may not have waited long enough to reach equilibrium and in some cases the purity and composition of the solid may not have been checked. Where a large number of solubility products are available, as for goethite and ferrihydrite, the values given in Table 9.4 correspond on the whole, to the best ones. Where only one or two values have been determined they are listed, even if there are reservations about their reliability.

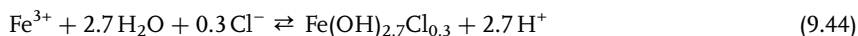
K_{so} values of the different Fe oxides range from 10^{-44} to 10^{-34} . The two least soluble (most stable) oxides are goethite and hematite. The K_{so} values given here suggest that hematite is less soluble than goethite and this conclusion is supported by some experimental evidence of Berner (1969) who found that in 0.01 M HCl at 85 °C, fine grained goethite is more soluble than hematite. The data in Table 9.4 suggest that the order of solubility is akaganéite > ferrihydrite > lepidocrocite > maghemite > goethite > hematite but it may also be hematite > goethite. In alkaline media there is experimental evidence that this order of solubilities is followed (Cornell and Giovanoli, 1990). The iron^{II} oxides are more soluble than the iron^{III} oxides with magnetite being more soluble than Fe(OH)₂.

The dissolution reactions for *goethite* are given in eq. (9.1) and (9.4). The $\log^*K_{so}$ value of 1.4 ± 0.8 listed here was obtained in 3 M NaClO₄ by Schindler et al. (1963) using the dissolution method. In fact the value lay between 0.6 and 2.2. The value of Bigham et al. (1995) obtained by precipitation agreed with this value but showed less variation between triplicates. Hsu and Marion (1985) also using the precipitation technique (and a 16 year equilibration time) obtained similar results.

Researchers in the aluminium industry have investigated the solubility of goethite in sodium aluminate and NaOH solutions. Basu (1983) found, using samples of natural goethite, that the equilibrium solubility of goethite in sodium aluminate solution was close to zero at room temperature and increased exponentially as the temperature rose above 100 °C. She also found that the isothermal solubility was greater in 5 M NaOH than in 5 M sodium aluminate solution; at 150 °C, for example, [Fe³⁺] was 20 and 50 mgL⁻¹, respectively.

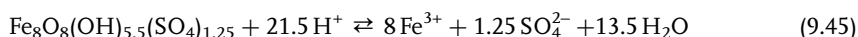
Only three values of $\log^*K_{so}$ are available for *lepidocrocite* and these are not in very good agreement. Hashimoto and Misawa (1973) measured the solubility of lepidocrocite produced by anodic deposition from Fe^{II} solution on a platinum electrode and obtained a value for $\log^*K_{so}$ of 2.50. This agrees with the value calculated from the free energy of formation (Blesa et al., 1994). Mohr et al. (1972) quote a value of 2.72 and Lindsay (1979) gives 1.59.

Biedermann and Chow (1966) followed the change in Fe_T and pH of partly hydrolysed (with NaHCO_3) FeCl_3 solution (in 0.5 M NaCl) at 25 °C over two months and confirmed by XRD that the product was *akaganéite*. As *akaganéite* contains up to 7% chloride in the structure, the formula was written as $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$. The data could be explained by assuming the following reaction,



The $\log *K_{\text{so}}$ value which is the only value available to date was found to be -3.04 ± 0.05 . The free energy of formation ($-752.7 \text{ kJ mol}^{-1}$) calculated from this $*K_{\text{so}}$ is very much lower than that of goethite which does not accord very well with the observed behaviour of the two oxides; this suggests that the equation chosen by Biedermann and Chow to describe their reaction may not in fact apply to *akaganéite*.

A log ion activity product of $\log *K_{\text{so}} = 17.4 \pm 0.1$ for *schwertmannite* based on the reaction:



was put forward by Bigham et al. (1995). This value is higher than the $\log *K_{\text{so}} = 10.5 \pm 2.5$ measured by Yu et al. (1999). The solubility of *schwertmannite* may depend on the sulphate content of the mineral (Yu et al., 2002). The values of $\log K_{\text{so}}$ for *ferrihydrite* range from -37 to -39 with a mean of around -39 ± 0.7 ($n = 11$) (Fox, 1988). The range of solubilities may be due to differences in age and the particle size of the samples: the particle size distribution is dependent upon pH (Lengweiler et al, 1961). For example, $\log *K_{\text{so}}$ decreased from 3.96 at 200 hr to 3.55 after one year of ageing (Schindler et al., 1963). Most reported studies appear to have been carried out on two line *ferrihydrite* and over a pH range of between 1.7 and 3.0. Recently, Yu et al. (2002) compared the solubilities of 2-line and 6-line *ferrihydrite* and found, as expected, that the latter is less soluble (Table 9.4).

Fox (1988) suggested that the K_{so} for *ferrihydrite* should be written as $[\text{Fe}] \cdot [\text{OH}]^{2.35}$ instead of $[\text{Fe}] \cdot [\text{OH}]^3$ as is customary. This suggestion was based on the following linear relationship (pH range 2–7),

$$-\log (\text{Fe}^{3+}) = 2.35 \text{ pH} - 1.17 \quad (n = 60; \quad r^2 = 0.994) \quad (9.46)$$

Equation (9.46) has a slope of 2.35 instead of 3.0 and implies that there are 0.65 moles of nitrate in the structure of *ferrihydrite*. The problem with this formulation is, however, that it refers to a salt, not an oxide hydroxide and thus, cannot apply to *ferrihydrite*. On the other hand, Byrne and Yu (2000) suggest that their $*K_{\text{so}} = [\text{Fe}][\text{OH}]^{-2.86}$ for freshly precipitated *ferrihydrite* has a non integral value owing to variations in the activity of the solid phase, which as mentioned earlier, is due to the influence of pH (3–7.5) on the particle size distribution of the precipitate. Two fairly similar K_{so} values of ca. -39 have been reported for “soil” *ferrihydrite* (Table 9.4). It is probable that in these soils, *ferrihydrite* determined the activity of dissolved Fe.

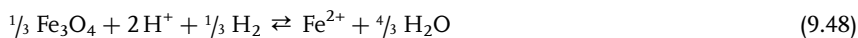
The solubility of *hematite* was measured in NaOH/NaCl (0.007–2 m) at between 60 and 300 °C at saturated water vapour pressure with the dissociation reaction being described by:



The value of $\log K_{s4} = -19.64 \pm 0.06$ at 60 °C and -14.82 ± 0.14 at 300 °C (Diakonov et al., 1999). Solubility rose with rising $[\text{OH}^-]$. In very concentrated solutions of NaOH or KOH, ion pairs can form between $\text{Fe}(\text{OH})_4^-$ and the cation and at temperatures > 200 °C, these ion pairs increase the solubility of hematite in such solutions. In alkaline media, the solubility of hematite depended upon the alkali hydroxide used in the order (Ishikawa et al., 1997):



Sweeton and Baes (1970) measured the solubility of well-crystallized *magnetite* in dilute acid and base at a H_2 partial pressure of 0.1 MPa and over a temperature range of 50–300 °C. The value of $\log^* K_{s0}$ of 12.02 corresponds to the reaction



Only Fe^{2+} and its hydrolysis products (FeOH^+ , $\text{Fe}(\text{OH})_2^0$ and $\text{Fe}(\text{OH})_3^-$) were considered to be important. Under more alkaline conditions and at high temperatures, oxidative dissolution occurs (Tremaine and Leblanc, 1980).

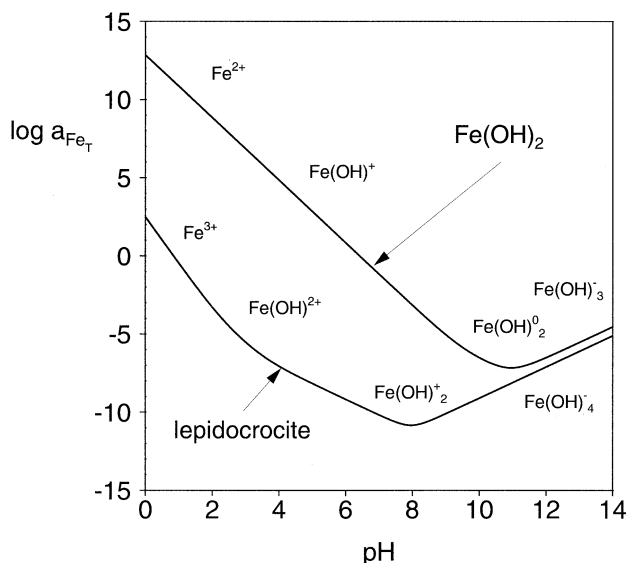


Fig. 9.9 Comparison between the solubility of $\text{Fe}(\text{OH})_2$ and that of lepidocrocite as a function of pH.

The values given in Table 9.4 for $Fe(OH)_2$ correspond to the reaction



The freshly precipitated $Fe(OH)_2$ showed broadened XRD lines and had a $\log K_{so}$ of -14 . With time a transformation to a more ordered phase with $\log K_{so}$ of -15.1 occurred. Figure 9.9 compares the solubility of $Fe(OH)_2$ with that of lepidocrocite as a function of pH.

10

Surface Chemistry and Colloidal Stability

10.1

Surface Functional Groups

With the exception of the massive crystals found in rocks, iron oxides usually exist as small crystals with dimensions ranging from a few microns down to a few tens of nanometres. Such particles have a high surface to volume ratio, hence a significant proportion of the atoms is located at the particle surface. It is largely the properties, particularly the surface free energy (of the order of tens of kJ mol^{-1}) of these surface atoms, that govern the behaviour of colloidal systems. Reactions at the iron oxide/solution interface influence crystallization and dissolution of these compounds, their stability and rheology and their interactions with adsorbing species.

Under dry conditions, surface Fe atoms may be coordinatively unsaturated: this was confirmed for heated ferrihydrite with EXAFS (Zhao et al., 1994). Because they carry unoccupied atomic orbitals surface Fe atoms are Lewis acids and react with Lewis bases¹⁾. In aqueous systems, therefore, they coordinate with hydroxyl ions or water molecules which share their “lone” electron pairs with Fe. Upon adsorption, the water molecules usually dissociate resulting in a surface covered by hydroxyl groups coordinated to the underlying Fe atoms. Hydroxylation of iron oxides is a fast reaction requiring minutes, or at most hours for completion. It is followed by further adsorption of water molecules which hydrogen-bond to the surface OH groups. The properties of the adsorbed water layers are different from those of bulk water; an “ice-like” structure has been suggested (Clarke and Hall, 1992). The density of hydrogen bonding appears to be greater than that of bulk water and the dielectric constant, which is very low in the first water layer, increases as the number of adsorbed water layers rises (Blyholder and Richardson, 1962; Jurinak, 1964, 1966; McCafferty and Zettlemoyer, 1970; Gast et al., 1974; Kuwabara et al., 1987; Tsugita et al., 1990; Kandori and Ishikawa, 1991; Clark and Hall, 1992; Joseph et al., 1999 a, b).

Adsorbed water promotes self adhesion of Fe oxide particles in powders (e.g. cosmetics) which can lead to problems with clumping (Tsugita et al., 1990).

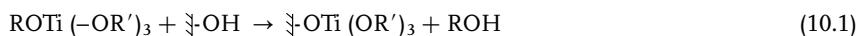
The surface hydroxyl groups (whether they arise from adsorption of water or from structural OH) are the *functional groups* of iron oxides, i.e. they are the chemically re-

1) A Lewis base is a molecule or atom (for example H_2O , NH_3 or pyridine) that can donate an

electron pair and will, therefore, react with Lewis acids such as metal cations.

active entities at the surface of the solid in an aqueous environment. They possess a double pair of electrons together with a dissociable hydrogen atom which enables them to react with both acids and bases. Iron oxides are, therefore, amphoteric (eq. 10.2 and 10.3).

The surface hydroxyl groups can be replaced by silane groups (Micale et al., 1985) or by titanate groups (Hotta et al., 1991) e.g.



where R and R' are alkyl groups and ≡ represents the oxide surface. Both the silane and the titanate groups make the surface hydrophobic (the particles can be dispersed in benzene, but not in water). Fractal analysis showed that surface roughness increased when hematite was titanated owing to the presence of the alkyl chains (Hotta et al., 1991).

Heat treatment at high enough temperatures removes the surface hydroxyl groups. Upon heating at several hundred °C in oxygen, the pairs of hydroxyl groups on the hematite surface condense to water which then desorbs, leaving behind an oxo bond (see Chap. 13). Exposure of the dehydroxylated hematite to water vapour leads to regeneration of these hydroxyl groups. If, however, hematite is heated at 800°C, irreversible sintering of the particles changes the number of potential hydroxyl sites per unit area and hence, the proportions of the different hydroxyl groups (Rochester and Topham, 1979a).

Crystallographic considerations indicate that the surface hydroxyl groups may be coordinated to one, two or three underlying Fe atoms. These singly, doubly and triply coordinated groups (Fig. 10.1) are sometimes also termed A, B or C type, respectively. If a charge of $+1/2$ is assigned to each Fe-O bond (assuming sixfold coordination) the three types of surface OH groups carry charges of $-1/2$, 0 and $+1/2$. The overall density of these groups depends on both the crystal structure and on the extent of development of the different crystal faces; it, therefore, varies to some extent from oxide to oxide and is also influenced by crystal morphology. A fourth type of group is the geminal group, i.e. two OH groups attached to one Fe atom. Table 10.1 lists the density of various groups for the more common crystal faces of goethite and hematite. For the (most reactive) singly coordinated groups, this is between 3 and 8 OH nm⁻² and for the total number between ca. 8 and 16 OH nm⁻².

The configurations of the various types of hydroxyls on common *goethite* planes are shown in Figure 10.2. All three types of hydroxyl groups coexist on the (001)

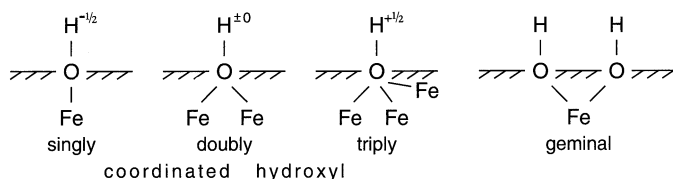


Fig. 10.1 Singly coordinated, doubly coordinated, triply coordinated and geminal surface hydroxyl groups on iron oxides.

Tab. 10.1 Hydroxyl density on different goethite and hematite faces (Barron and Torrent, 1996, with permission).

Face		Singly coordinated groups/nm ⁻²	Doubly coordinated groups/nm ⁻²	Triply coordinated groups/nm ⁻²	Singly coordinated pairs/nm ⁻²
Goethite	[101]	3.0	3.0	9.1	1.5
	[210]	8.2	8.2	–	4.1
	[100]	7.2	7.2	–	3.6
	[001]	3.3	3.3	–	1.7
Hematite	[100]	5.8	2.9	–	2.9
	[110]	5.0	5.0	5.0	2.5
	[012]	7.3	–	7.3	3.7
	[104]	5.3	5.3	5.3	–
	[018]	–	6.3	3.2	–
	[113]	4.1	4.1	8.3	2.1
	[001]	–	13.7	–	–

plane, whereas singly and doubly coordinated groups are present on (100) and only singly coordinated hydroxyls on (010). In real crystals, it is the (101) and to a lesser extent, the (210) plane, that occurs most frequently (see Fig. 4.4 and 4.5). All three types of hydroxyl are found on (101) (Fig. 10.2), whereas on the (210) faces, there are only singly and doubly coordinated groups. Equal numbers of singly and triply coordinated hydroxyls are present on the (001) plane of *lepidocrocite*, but on the predominant (010) plane, there are only doubly coordinated groups. The configurations of the common crystal faces of *hematite* are shown in Figure 10.3. The rhombohedral planes (104) and (012) and the prismatic planes (110) and (100) carry singly coordinated FeOH groups (arranged in pairs), whereas the basal plane (001) has only doubly coordinated groups.

Owing to differences in the numbers of underlying Fe atoms that are coordinated to the surface functional groups, the acidity and hence, the reactivity of the different types of hydroxyl groups should vary. Adsorption and charging studies appear to indicate that the doubly coordinated surface hydroxyls on goethite, hematite and lepidocrocite are inert over a wide pH range (Russell et al., 1974; Lewis & Farmer, 1986; Hiemstra et al., 1989; Hiemstra & Van Riemsdijk, 1996). Both scanning field microscopy data (Jordan & Eggleston, 1998) and titration data (Hiemstra & Van Riemsdijk, 1999) suggest that, as only doubly coordinated groups are present on the (001) plane of hematite, this face is unreactive except at the extremes of pH: it does not contribute to the charging of the crystal between pH 4 and pH 10 and it does not adsorb phosphate (Colombo et al., 1994) or sulphate (Sugimoto & Wang, 1998). Where this plane does appear to be reactive, it is probably not a pure (001) face, but instead has defects and steps on it and hence other types of surface hydroxyls (Hiemstra & Van Riemsdijk, 1999). On goethite the charging reactions (see section 10.1) involve singly and triply coordinated surface groups: the triply coordinated hydroxyls are of two kinds with different proton affinities which are related to structural differences

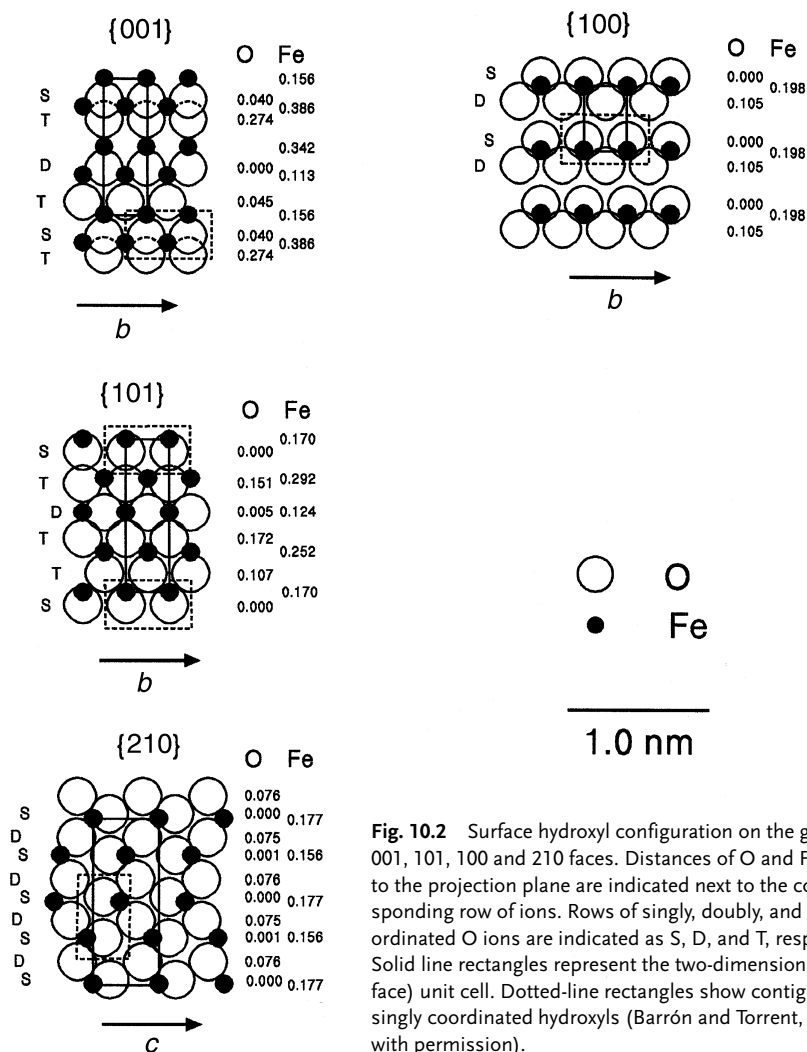


Fig. 10.2 Surface hydroxyl configuration on the goethite 001, 101, 100 and 210 faces. Distances of O and Fe ions to the projection plane are indicated next to the corresponding row of ions. Rows of singly, doubly, and triply coordinated O ions are indicated as S, D, and T, respectively. Solid line rectangles represent the two-dimensional (surface) unit cell. Dotted-line rectangles show contiguous singly coordinated hydroxyls (Barrón and Torrent, 1996, with permission).

(Venema et al., 1998). Adsorption of ions on Fe oxides is considered to involve only the singly coordinated surface groups.

The different kinds of functional groups give rise to several bands in the infrared spectrum (see Chap. 7). In general, bridging of OH groups across two or three Fe atoms to produce double or triple coordination, progressively shifts the stretching vibration to lower wavenumbers (Rochester and Topham, 1979 a). *In vacuo*, the singly coordinated OH groups on goethite are responsible for an IR band at 3486 cm^{-1} which upon deuteration, shifts to 2700 cm^{-1} and upon adsorption of phosphate ions, disappears (Russell et al., 1974; Parfitt et al., 1976). Ford and Bertsch (1999) allocated a series of weak endothermal effects noted during TG analysis of goethite to the different functional groups.

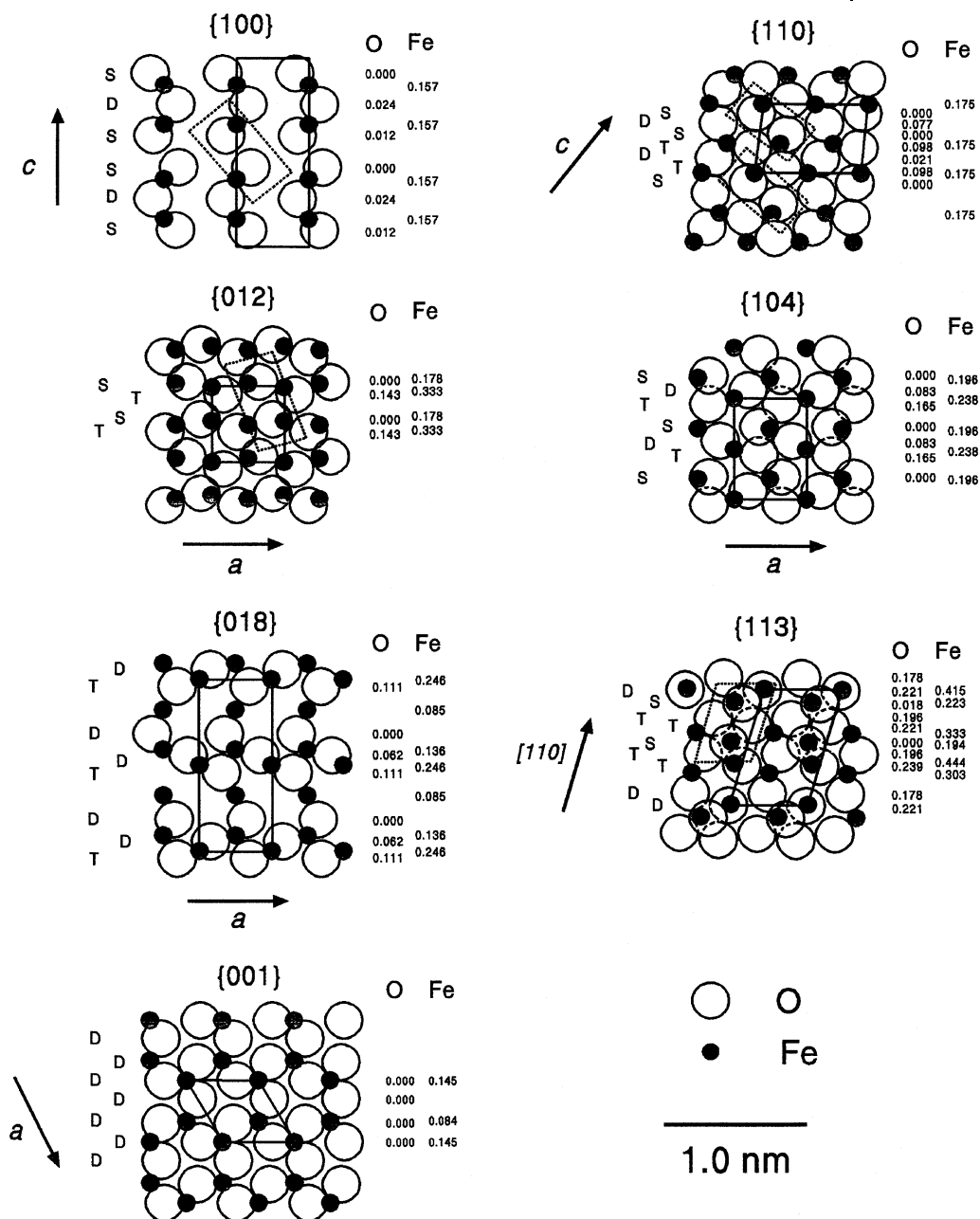


Fig. 10.3 Surface hydroxyl configuration of the hematite [100], [110], [012], [104], [018], [113], and [001] faces. Distances of O and Fe ions to the projection plane are indicated next to the corresponding row of ions. Rows of singly, doubly and triply

coordinated O ions are indicated as S, D, and T, respectively. Solid-line rectangles represent the two-dimensional (surface) unit cell. Dotted-line rectangles show contiguous singly coordinated hydroxyls (Barrón and Torrent, 1996, with permission).

The density of surface functional groups on various Fe oxides has been measured by such techniques as acid/base titration, BET treatment of water vapour isotherms, D₂O or tritium exchange and by reaction with adsorbing species such as fluoride, phosphate or oxalate (Table 10.2). Another method involves drying to remove physically adsorbed water followed by reaction with CH₃MgI (Grignard reagent) and measurement of the amount of this reagent that has been consumed (Boehm, 1971; Tamura et al., 1999). Recently, adsorption of methanol has been used to determine the number of surface active sites on a wide range of oxides including hematite (Badlani and Wachs, 2001).

There are, unfortunately, wide discrepancies between the results obtained by different methods. These can, in the first place, reflect differences between different samples of a particular oxide. Furthermore, the number of functional groups corresponding to the maximum uptake of the adsorbed species depends on such factors as the size of the adsorbate, the density and arrangement of the functional groups, the pH of

Tab. 10.2 Experimentally determined density of OH groups on the different iron oxides.

Oxide	No. of OH groups (nm⁻²)	Method of determination	Source
Goethite	6	acid/base titration	Huang, 1971
	16.8 ^{a)}	surface crystal structure	Yates, 1975
	4	acid/base titration	Sigg and Stumm, 1981
	7.3	excess F ⁻ at pH 5.5	Sigg and Stumm, 1981
	2.6 ^{b)}	acid/base titration	Balistreri and Murray, 1981
	0.8	phosphate adsorption	Hansmann and Anderson, 1985
	1.5	SeO ₃ ²⁻ -adsorption isotherm	Hansmann and Anderson, 1985
	18 ^{a)}	surface crystal structure	Hsi and Langmuir, 1985
	2.9	phosphate adsorption	Torrent et al., 1990
Lepidocrocite	1.68	acid/base titration	Lovgren et al., 1990
	8	acid/base titration	Waite and Morel, 1984
	9.6	F ⁻ adsorption	Davies and Morgan, 1989
	1.68	acid/base titration	Zhang et al., 1992
Ferrihydrite	11.4	isotope exchange	Yates, 1975
	1.97	acid/base titration	Charlet and Manceau, 1992
Hematite	4.4	chemical reaction	Boehm, 1971
	9.1	CH ₂ N ₂ adsorption	Boehm, 1971
	5.5–10	IR and H ₂ O adsorption	Yates, 1975
	5.5–9 ^{b)}	surface crystal structure	Yates, 1975
	22.4	isotopic exchange	Yates, 1975
Magnetite	0.35–4.2	phosphate adsorption	Barrón et al., 1988
	5	NaOH	Tamura et al., 1983
	5.2	acid/base titration	Sun et al., 1998
Maghemite	5.1–9.8	weight loss at 200 °C	Garcell et al., 1998

a) Calculated

b) Calculated by Lovgren et al. (1990) from data in the publication

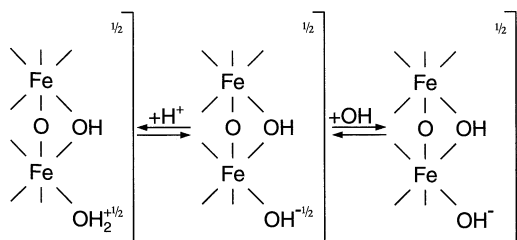


Fig. 10.4 Development of charge at the Fe-oxide/solution interface.

the system and the duration of the reaction. The *fluoride* ion method yields a particularly high site density owing to the ion's small size and strong nucleophilic character and to the strong Fe-F bond, all of which promote uptake. Hiemstra and van Riemsdijk (2000), however, could not find a well defined maximum for fluoride adsorption on goethite and concluded that this ion should not, therefore, be used as a probe for the density of surface OH groups. The measurement of site density by *phosphate* adsorption takes into account the fact that one phosphate ion is coordinated to two adjacent, singly coordinated OH groups on goethite. Adsorption of phosphate on 31 synthetic goethites with different crystal morphologies and sizes was $2.51 \pm 0.17 \mu\text{mol m}^{-2}$ which is in good agreement with the presence of one singly coordinated hydroxyl group per unit cell ($0.341/\text{nm}^2$) on the predominant 101 plane (Torrent et al., 1990).

Data from a number of acid/base titration studies suggested that reasonable values for the average density of OH groups on goethite, lepidocrocite and ferrihydrite are 1.4–1.68 (Lovgren et al., 1990; Ali and Dzombak, 1996), 1.67 (Zhang et al., 1992) and 1.97 sites nm^{-2} (Charlet and Manceau, 1992), respectively. Tamura et al. (1999) and Hiemstra and van Riemsdijk (2000) consider, however, that the low site density obtained by potentiometric titration may be the result of the difficulty of reaching site saturation, even at very low pH, owing to increased lateral interactions between charged sites. Blesa et al. (2000) commented that site densities should not be determined by fitting acid/base titration data unless the titration curves exhibit clear saturation with protons. Christl and Kretzschmar (1999) used a range of site densities when modelling competitive adsorption of cations on hematite and found that good agreement with the experimental data was obtained using 5–10 sites nm^{-2} .

The overall density of surface functional groups can be determined from crystallographic data provided that the specific surface area of the sample and the crystal morphology can be determined accurately. The extent of development of the different crystal faces can be found by means of electron microscopy, but only if the crystal morphology is sufficiently well expressed.

10.2

Surface Acidity and Acidity Constants

Charge on the oxide surface is established by dissociation (ionization) of the surface hydroxyl groups. The situation corresponds to adsorption or desorption of protons depending on the pH of the solution (Fig. 10.4). These reactions can be trea-

ted as acid/base equilibria and in the classical, one site, two constants ($\text{p}K_{\text{a}}$ values) model, they are represented by the following dissociation reactions ($\equiv$ denotes the surface):



Eq. (10.3) can equally well be regarded as a reaction of protons from the surface hydroxyls with hydroxyl ions from solution.

The equilibrium constants for these reactions are termed conditional (see below) acidity or stability constants, K_{a}^{s} , or sometimes, proton affinities:

$$K_{\text{a}1}^{\text{s}} = \frac{\{\equiv\text{FeOH}\}[\text{H}^+]}{\{\equiv\text{FeOH}_2^+\}} \text{ mol dm}^{-3} \quad (10.4)$$

$$K_{\text{a}2}^{\text{s}} = \frac{\{\equiv\text{FeO}^-\}[\text{H}^+]}{\{\equiv\text{FeOH}\}} \text{ mol dm}^{-3} \quad (10.5)$$

where $\{\}$ = surface species and $[\]$ = solution species.

Adsorption and desorption reactions of protons on iron oxides have been measured by the pressure jump relaxation method using conductimetric titration and found to be fast (Tab. 10.3). The desorption rate constant appears to be related to the acidity of the surface hydroxyl groups (Astumian et al., 1981). Proton adsorption on iron oxides is exothermic; potentiometric calorimetric titration measurements indicated that the enthalpy of proton adsorption is -25 to -38 kJ mol^{-1} (Tab. 10.3). For hematite, the enthalpy of proton adsorption is $-36.6 \text{ kJ mol}^{-1}$ and the free energy of adsorption, $-48.8 \text{ kJ mol}^{-1}$ (Lyklema, 1987).

The acidity constant, K_{a}^{s} , is related to the free energy of adsorption, ΔG_{ads} , by the expression, $\Delta G_{\text{ads}} = -RT \ln K_{\text{a}}^{\text{s}}$, which rearranges to give

$$K_{\text{a}}^{\text{s}} = \exp(-\Delta G_{\text{ads}}/RT) \quad (10.6)$$

Tab. 10.3 Enthalpies of adsorption and kinetics of proton adsorption and desorption on iron oxides.

Oxide	Rate of adsorption ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	Rate of desorption (s^{-1})	ΔH_{ads} (kJ mol^{-1})	Reference
Goethite	–	–	-38.9 (pzc) -29.6 (pH 4)	Machesky and Anderson, 1986 Zeltner et al., 1986
Hematite	$2.4 \cdot 10^{-5}$	0.16	– -29 (KCl) -25 (KNO_3)	Astumian et al., 1981 Szczypa et al., 1994 Szczypa et al., 1994
Magnetite	$1.4 \cdot 10^{-5}$	0.34	–	Astumian et al., 1981

The free energy of interaction of protons (and other ions) with a charged surface is the sum of the chemical energy of adsorption and an electrostatic component, i.e.

$$\Delta G_{\text{ads}} = \Delta G_{\text{chemical}} + \Delta G_{\text{coulombic}} \quad (10.7)$$

therefore,

$$-RT \ln K_{\text{cond}}^{\text{s}} = -RT \ln K_{\text{int}}^{\text{s}} + zF\psi_0 \quad (10.8)$$

hence

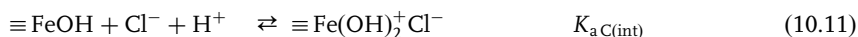
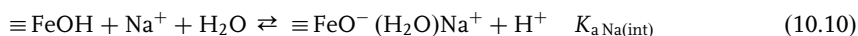
$$K_{\text{a int}}^{\text{s}} = K_{\text{a cond}}^{\text{s}} \cdot \exp(-zF\psi_0/RT) \quad (10.9)$$

where $K_{\text{int}}^{\text{s}}$ = intrinsic acidity constant; z = the charge of the adsorbed species; F is the Faraday constant and ψ_0 is the surface potential. Hence, the acidity constants for surface hydrolysis reactions, unlike the acidity constants for the solution reactions, incorporate both a mass balance and an electrostatic term; the latter refers to the free energy required to take a proton from a charged surface at a potential ψ_0 through a potential gradient to the bulk solution.

The *conditional* acidity constant, $K_{\text{cond}}^{\text{s}}$, is obtained by combining acid/base titration data with the site density. The charge on the oxide surface influences the acidity of the surface hydroxyl groups; the higher (lower) the positive charge at the surface, the more difficult (easier) it is to adsorb (remove) protons. The acidity constants are, therefore, not constant, but depend on the surface charge, i.e. on the degree of ionization of the OH groups and on the ionic strength of the solution.

Intrinsic acidity constants ($K_{\text{a int}}^{\text{s}}$) represent the dissociation of surface hydroxyl groups at zero surface charge. These constants cannot be measured directly. They are obtained from the experimentally accessible conditional constants, $K_{\text{cond}}^{\text{s}}$, either by extrapolation to a situation of zero surface charge, or by fitting the experimental data to an appropriate double layer model (section 10.3) to compute the electrostatic component.

In addition to proton adsorption, interactions between the ions of the inert electrolyte (counter ions, section 10.3) and the oxide surface lead to ion pair formation which influences the electrochemical properties of the oxides and the determination of $\text{p}K_{\text{a}}$ values. Ion pair formation involves outer sphere surface complexes (see Chap. 11), e.g.



The equilibrium constants for ion pair formation are formulated in the same way as those for proton adsorption; some values for the iron oxides are listed in Table 10.4.

The acidity constants for the surface protolysis reactions provide a measure of the extent to which the reaction will proceed. For the iron oxides the values of the $\text{p}K_{\text{a}}$ s usually fall between 5 and 10, but there is considerable variation in the values for dif-

Tab. 10.4 Stability constants for ion pair formation on goethite and hematite.

Oxide	$pK_{\text{anion}}^{\text{int}}$	$pK_{\text{cation}}^{\text{int}}$	Electrolyte	Reference
Goethite	6.2 ± 0.3	9.0 ± 0.3	KNO ₃	Yates, 1975
	7.5 ± 0.3	9.3 ± 0.05	NaNO ₃	Smith and Jenne, 1991
	6.2 ± 0.6	9.3 ± 0.05	KCl	Smith and Jenne, 1991
	8.49	9.64	0.1 M NaCl	Lumsdon and Evans, 1994
Hematite	7.5 ± 0.3	9.5 ± 0.3	KCl	Breeuwsma, 1973

Tab. 10.5 Acidity constants of the iron oxides.

Oxide	$pK_{a1(\text{int})}$	$pK_{a2(\text{int})}$	Reference
Goethite	4.2	10.5	Yates, 1975 ^{a)}
	6.0	—	Astumian et al., 1981
	7.47	9.51	Lovgren et al., 1990
	6.7	9.0	Müller and Sigg, 1992
	7.09	11.11	Lumsdon and Evans, 1994
Lepidocrocite	5.7	7.7	Waite and Morel, 1984
	6.4	8.3	Davies and Morgan, 1989
	6.45	8.13	Zhang et al., 1992
Ferrihydrite	6.6	9.1	Farley et al., 1985
	7.29	8.39	Dzombak and Morel, 1990
	6.93	8.12	Hansen et al., 1994
Hematite	8.86	10.1	Huang, 1971
	6.7	10.1	Breeuwsma, 1973
	5.8	11.1	Breeuwsma, 1973 ^{a)}
Magnetite	5.6	—	Astumian et al., 1981
	5.6	—	Regazzoni et al., 1983
	4.3	8.3	Marmier et al., 1999
Maghemite	3.8	9.4	Garcell et al., 1998

a) Values recalculated by James and Parks (1982) using the double extrapolation method.

ferent samples of a particular oxide (Tab. 10.5). A major cause of the range of reported pK_a s is the variation in the site density chosen when modelling proton adsorption. Smith and Jenne (1991) point out that changing the site density for the same sample of goethite from 16.8 sites nm⁻² to 2.6 sites nm⁻² changed the pK_{a1} from 4.9 to 5.6 and the pK_{a2} from -10.4 to -9.5.¹⁾ Further variations in pK_a are possible when the intrinsic acidity constant is estimated with the aid of a model; the values obtained depend to some extent on the double layer model chosen and on its underlying assumptions (James and Parks, 1982; Davis and Kent, 1990). A further factor is whether ion pairing of the counter ions has been taken into account. The

¹⁾ The sign depends on how the charging equations are written.

double extrapolation method (Davis and Leckie, 1978), which utilizes counter ion pairing, enables intrinsic acidity constants with a greater degree of self consistency to be obtained. More recently a modified, least squares pK_a spectrum approach (i.e. titration data have been fitted to a continuous site binding model) has been used with some success to obtain pK_a s for ferrihydrite (Smith and Ferris, 2001).

Various approaches have been used to calculate acidity constants from first principles. This is an area which appears to be developing rapidly. At present, there is often some divergence between the pK_a values obtained by the different approaches. Some of the most extensive investigations have been made by Van Riemsdijk and his co-workers in the Netherlands. Initially they suggested that the surface hydroxyl groups are involved in a one step, protonation reaction over a fairly narrow pH range and hence, are characterized by one pK_a value (Van Riemsdijk et al., 1986). Borkovec (1997) and also Boily et al. (2001) have compared this model with the two pK_a model and concluded that each model can provide a good approximation to the ionization behaviour of the oxide/water interface. Subsequently, the Dutch school developed the multisite complexation (MUSIC) model for proton adsorption with one proton adsorption reaction and one discrete acidity constant for *each* type of surface group (Hiemstra et al., 1989; 1989a; Hiemstra and Van Riemsdijk, 1996, 1999). In this model the pK_a values for each surface group are derived from both ligand interactions and either Pauling (Pauling, 1929) or in the modified model, actual, bond valences (Venema et al., 1998). In the MUSIC model, the different surface sites can have fractional charges. For goethite, for example, the singly, doubly and triply coordinated sites are written as $\text{FeO}^{-3/2}$ (or $\text{FeOH}^{-1/2}$), Fe_2OH^0 and $\text{Fe}_3\text{O}^{-1/2}$, respectively and on hematite the sites are $\text{FeO}^{-3/2}$, Fe_2O^{-1} and $\text{Fe}_3\text{O}^{-1/2}$. The calculated pK_a s are combined with information about the extent of development of the different crystal planes and the number of different surface groups/plane and used in a model of the electrical double layer (see section 10.3) to predict the surface charging curves for the oxides. Venema et al. (1998) found reasonably good agreement with the experimental curves for goethite and lepidocrocite: for hematite the predictions were less satisfactory owing to some uncertainties concerning the morphology. Boily et al. (2001) also obtained charging curves for different samples of goethite using the MUSIC model, but taking surface relaxation effects into account. They concluded that although the interdependency of the modelling parameters made determination of a unique set of constants difficult, the concept of different surface functional groups is realistic. A further attempt to relate pK_a s to the properties of the bulk crystal has been made by Sverjensky and coworkers (see section 10.4). The use of molecular dynamics and molecular calculations for clusters has also been applied to the evaluation of pK_a values (Rustad et al., 1996; 1999). To date, the agreement between the proton affinities for the groups on goethite found by this method and with the MUSIC model has not been particularly good (Hiemstra and Van Riemsdijk 1999).

10.3

The Electrical Double Layer and Electrochemical Properties

The charge on the solid that arises as a result of the ionization of the surface hydroxyl groups is balanced by a layer of counter ions (from the electrolyte) of opposite charge located in the aqueous phase: this ensures that the interfacial region is electrically neutral. The charged surface, together with the layer of counter ions in the solution phase make up what is termed the electrical double layer (edl). The separation of charges in the edl results in the development of a difference in potential between the surface and the solution: the surface charge density, σ , (coulombs m^{-2}) can be related to the potential gradient, ψ , by a suitable molecular model. In the simplest of these, the Helmholtz model, the charge on the solid and the potential across the edl are related by the capacitance, C (Farads), i.e. $\sigma = C\psi$, as in a parallel plate capacitor. As the charge on (Fe) oxides arises from the preferential adsorption of protons and hydroxyl ions, these ions are commonly termed *potential determining* or, as suggested by Lyklema (1991), *surface* ions.

The earliest models used to describe the distribution of charges in the edl are, besides the Helmholtz model, the Gouy-Chapman diffuse layer model and the Stern-Graham model. Details of these models are given in Westall and Hohl (1980), Schindler (1981, 1984) and Schindler and Stumm (1987).

Their electrochemical properties serve to regulate the coagulation rates, catalysis behaviour and electron transfer reactions of iron oxides (Mulvaney et al., 1991). Two major methods of characterizing electrochemical behaviour are potentiometric titration and electrophoresis.

Acid/base potentiometry enables the surface charge density to be measured. This involves comparison of the titration curves obtained for the suspension of oxide at several different ionic strengths (10^{-3} – 10^{-1}M) with that of the electrolyte alone, followed by calculation of the net consumption of protons or hydroxyl ions (mol g^{-1}) at each pH. The data is presented as a plot of excess of acid or base ($\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}$) mol g^{-1} or mol m^{-2} vs pH (adsorption isotherm) or as a plot of surface charge, σ , (coulombs m^{-2}) vs pH (charging curve) (Figure 10.5).

The titrations should be carried out slowly enough (e.g. 0.01 pH units per 5 min) to ensure that equilibrium is reached at each step and hysteresis thus avoided; hysteresis is a particular problem with ferrihydrite (Yates, 1975; Davis and Leckie, 1978) as is partial dissolution of the solid in the acid range. It is also essential to exclude CO_2 from the system (by outgassing with N_2) because CO_2 adsorbs on iron oxide surfaces, raises the negative surface charge and lowers the point of zero charge (section 10.4) (Zeltner and Anderson, 1988; Lovgren et al., 1990; Lumsdon and Evans, 1994). Adsorption of CO_2 is particularly pronounced for goethites produced in alkaline solutions. Discrepancies between the results of different workers can be attributed to these experimental problems. A further complication with magnetite and the ferrites is magnetic coagulation. Special cell design and control over the stirring rate and suspension concentration is required to overcome this problem (Ardizzone et al., 1982).

Electrophoresis involves movement of particles in suspension under the influence of an electric field; the direction of movement depends on the charge of the particles

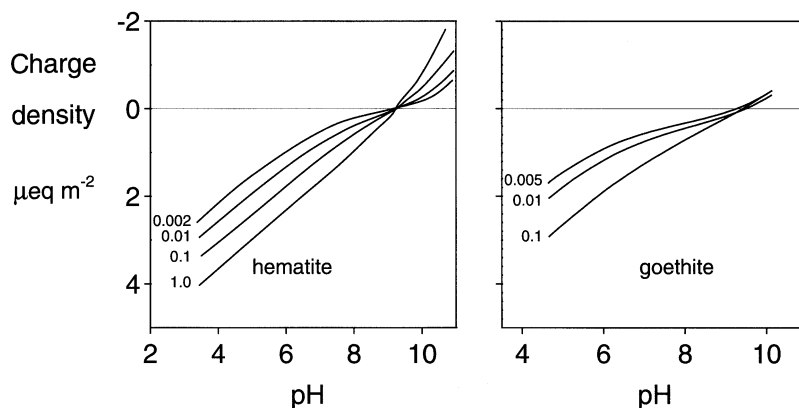


Fig. 10.5 Surface charge density of hematite and goethite as a function of pH in an inert electrolyte of various concentrations (KCl for hematite; NaNO₃ for goethite) as obtained by acid/base titration (hematite: Atkinson et al., 1967, with permission; goethite: S. Glasauer, unpubl.).

with a negative particle migrating to the cathode and a positively charged particle moving towards the anode. The charge on the particles and hence the direction of movement depends on the pH of the suspension; the pH at which there is no movement equals the isoelectric point (see section 10.4). The solution adjacent to the charged particle surface is more viscous than the bulk and so moves with the particles, i.e. each particle is surrounded by an envelope of associated water. A shear plane between the moving and stationary phases is created within the electrical double layer, but at some distance from the particle surface. Movement of the particle relative to the bulk creates a separation of charges, hence a potential difference termed the zeta potential develops at the shear plane. The zeta potential cannot be measured directly. It is calculated from the electrophoretic mobility of the particles. Either this mobility or the zeta potential itself is then plotted against pH (Fig. 10.6). The accuracy of conversion of electrophoretic mobility to potential depends in part on the particle shape (James and Parks, 1982). Self-consistent model calculations of surface charge from electrokinetic potential are possible for hematite because this compound can be prepared as monodispersed spheres. The calculations for goethite are far less reliable owing to the acicular shape of the crystals; more success would be anticipated with subrounded crystals of goethite (Cornell et al., 1991).

Particle mobility and zeta potential can now be measured by more sophisticated techniques. With *photoelectrophoresis*, particle mobility is measured as a function of pH under the influence of ultraviolet radiation. At pH < 8, the electrophoretic mobility of irradiated hematite particles ($\lambda = 520$ nm) was markedly different from that measured in the absence of UV irradiation. This was attributed to the development of a positive surface charge induced by photo-oxidation of the surface Fe-OH^o sites to (Fe-OH)⁺ sites (Zhang et al., 1993). The *electroacoustic* technique involves generation of sound waves by the particles in the colloidal dispersion and from this data,

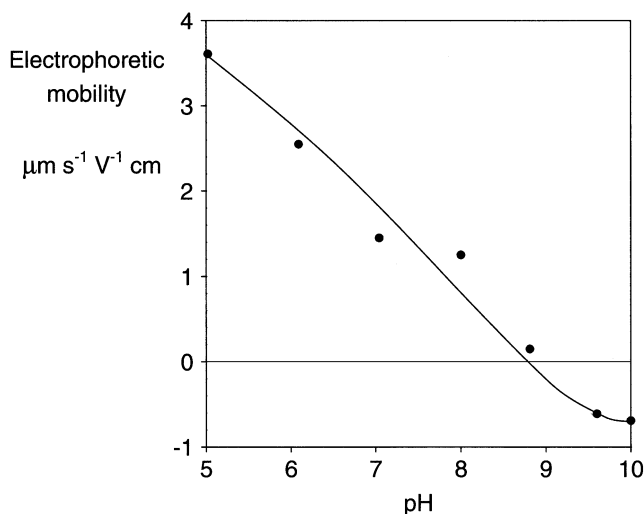


Fig. 10.6 Electrophoretic mobility of goethite vs. pH in 0.01 M NaNO_3 (S. Glasauer, unpubl.).

the zeta potential can be calculated. A feature of this method is that it can provide information about surface charge up to pH 12 and at ionic strengths of up to 3 M (Rowlands et al., 1997). The iep of goethite (9.4) found using this technique (in 0.01–0.6 M NaNO_3) was comparable to that found by conventional electrophoresis (Boily et al., 2001). The electrokinetic properties of goethite have also been investigated with *low frequency dielectric spectroscopy*; the potential estimated by this method was higher than that obtained from electrophoretic mobility data (Kiljstra et al., 1993). The difference between the results of the two methods was attributed to conduction by ions within the shear plane. This work and also the fact that the electrokinetic potential of iron oxides is always lower than the surface potential calculated from titration data, suggests that the classical electrokinetic model, which is formulated in terms of the diffuse double layer, cannot fully explain the electrokinetic behaviour of oxides.

Most investigators have concentrated on the electrochemical properties of hematite (Onoda and De Bruyn, 1966; Breeuwsma and Lyklema, 1971; Fokkink et al., 1989; Delgado and Gonzalez, 1998), ferrihydrite (Davis and Leckie, 1978; Dzombak and Morel, 1990) and goethite (Evans et al., 1979; Hiemstra and Van Riemsdijk, 1996; Boily et al., 2001) (see Tables 10.2, 10.5 and 10.6 for further references). There are fewer studies on magnetite (Tewari and McLean, 1972; Regazzoni et al., 1983; Ardizzone et al., 1982, 1987), lepidocrocite (Gupta, 1976; Zhang et al., 1992; Sun et al., 1992; Venema et al., 1998) and maghemite (Garcell et al., 1998). The reported surface charge density of goethite 2–3 pH units away from the point of zero charge (see 10.4) ranges from 0.07 to 0.19 coulombs m^{-2} (Lumsdon and Evans, 1994 and references therein). Variations depend upon whether CO_2 was excluded from the system (the presence of CO_2 leads to higher surface charge densities) and on the edl model to which the titration data is fitted: the capacitance values used in the models

Tab. 10.6 Isoelectric points and points of zero charge of iron oxides.

<i>Oxide</i>	<i>iep</i>	<i>pzc</i>	<i>Reference</i>
Goethite	–	7.5	Yates et al., 1975
	7.4	–	Tipping and Cook, 1982
	8.5	8.9	Hsi and Langmuir, 1985
		9.2	Lumsdon and Evans, 1994
	9.4	9.5	Hiemstra and Van Riemsdijk, 1996
	8.4		Blesa et al., 1997
	9.4*	–	Boily et al., 2001
Lepidocrocite	–	7.45	Gupta, 1976
	–	6.7	Waite and Morel, 1984
	–	7.29	Zhang et al., 1992
Akaganéite	7.3	–	Matijevic and Scheiner, 1978
	6.4	–	Rubio and Matijevic, 1979
	7.2	7.2	Kanungo, 1994
Ferrihydrite	–	7.9	Davis and Leckie, 1979
	–	7.8	Charlet and Manceau, 1992
Hematite		8.5	Parks and De Bruyn, 1962
	–	9.48	Huang, 1971
	7.0	–	Chang et al., 1983
	7.2 (synth.)	7.5	Hsi and Langmuir, 1985
	7.0 (nat.)	7.8	Hsi and Langmuir, 1985
	9.3	9.5	Penners et al., 1986
	8.5	8.5	Liang and Morgan, 1990
	9.5	9.5	Schudel et al., 1997
Magnetite		8.5–8.8 [#]	Jordan and Eggleston, 1998
	6.8	–	Tewari and McClean, 1972
	–	7.1	Astumian et al., 1981
	6.2	6.4	Ardizzone et al., 1982
	6.0	–	Sun et al., 1998
	–	6.3	Marmier et al., 1999
Maghemite	6.6	6.6	Garcell et al., 1998
CoFe ₂ O ₄	8.2	8.2	Ardizzone et al., 1987
		6.5	de Vincente et al., 2000

* measured with the Acoustosizer. # measured with the scanning force microscope.

are between 0.4 and 1.4 Farads m^{−2} (Lovgren et al., 1990; Lumsdon and Evans, 1994). Hiemstra and Van Riemsdijk (1996) noted that the charging capacity of goethite also appears to depend upon the method of preparation with their low surface area samples having a higher measured capacitance than did the high area ones. They suggested that this effect may depend upon whether the crystals are multi or monodomainic. Penners and Koopal (1986) reported that the charging behaviour of hematite also appeared to depend upon the method of precipitation: hematite grown in an autoclave had a lower surface charge per unit area, than did that

formed by forced hydrolysis at atmospheric pressure. They suggested that some ferrihydrite might have been present on the surface of the latter (lower temperature) sample. Another possibility is the contamination of the surface with chloride ions (Hesleitner et al., 1991) or the presence of a small amount of goethite in the sample. The electrochemical behaviour of hematite spheres coated with Y_2O_3 was, as would be expected, close to that of the coating rather than the core material (Plaza et al., 2001). Hesleitner et al. (1991) reported that lowering the permittivity of the solvent (water) by the addition of 50% methanol or ethanol to the system reduced the measured zeta potential of hematite: this effect was attributed to an increase in the association of the counter ions.

10.4

Point of Zero Charge

The total charge of the Fe oxide surface has several components, i.e.

$$\sigma_{\text{tot}} = \sigma_{\text{H}^+} + \sigma_{\text{IS}} + \sigma_{\text{OS}} \quad (10.12)$$

where σ_{H^+} represents the charge due to the adsorbed potential determining ions (net proton charge) and σ_{IS} , σ_{OS} refer to the charge due to inner and outer sphere adsorbing ions (see Chap. 11). For each iron oxide there is a pH at which the charge on the surface arising from all sources is zero: this is termed the pristine point of zero charge, ppzc (Bolt and Van Riemsdijk, 1982). This pH is also often referred to as the point of zero charge (pzc) or the isoelectric point (iep), but these terms can only be used interchangeably, if there is no specific adsorption.

The isoelectric point is the pH at which the net surface charge is zero, i.e. the positive and negative charges arising from *all* sources are equal, i.e.

$$\sigma_+ = \sigma_- \quad (10.13)$$

It is measured by electrophoresis (see section 10.3) and corresponds to the pH at which there is no motion of the particles in an electric field (Fig. 10.6).

The point of zero charge is the pH at which net adsorption of potential determining ions on the oxide is zero. It is also termed the point of zero net proton charge (pznpc). It is obtained by potentiometric titration of the oxide in an indifferent electrolyte and is taken as the pH at which the titration curves obtained at several different electrolyte concentrations intersect (Fig. 10.5). It is, therefore, sometimes also termed the common point of intersection (cpi). The pzc of hematite has been determined *directly* by measuring the repulsive force between the (001) crystal surface and the (hematite) tip of a scanning atom force microscope, as a function of pH: the pzc of 8.5–8.8 was close to that found by potentiometric titration (Jordan and Eggleston, 1998). This technique has the potential to permit measurement of the pzc of individual crystal faces, but the authors stress that the precision must be improved.

The pzc is related to the intrinsic acidity constants, by

$$\text{pH}_{\text{pzc}} = 1/2 (\text{p}K_{\text{a1(int)}} + \text{p}K_{\text{a2(int)}}) \quad (10.14)$$

It provides an estimate of the acidity of the oxide surface. In general, iron oxides have pzc's in the pH range 6–10 (Table 10.6). They are less acidic than SiO_2 and MnO_2 ($\text{pzc} < 3$) and similar to the Al oxides (pzc around 9). The pzc of goethite is close to the upper end of the range, whereas those of magnetite and maghemite are at the lower end.

It is important to realize that negative, positive and neutral functional groups can coexist on the oxide surface. At pH's $< \text{ppzc}$, the FeOH_2^+ groups predominate over the FeO^- groups, i.e. although the surface has a net positive charge, some FeO^- groups are still present (Figure 10.7). At the ppzc, the number of FeOH_2^+ groups equals the number of FeO^- groups and as the pH increases, the number of FeO^- groups increases.

Sverjensky (1994) and Sverjensky and Sahai (1996) proposed a method of calculating proton stability constants and hence, the point of zero charge, based on the properties of the bulk crystal structure. In extending an earlier attempt by Parks (1965) and subsequently by Yoon et al. (1979) to do this, they combined their electrostatically based crystal chemistry approach with a solid state solvation theory. The strength of proton binding is expressed as a function of both the average dielectric constant of the bulk solid, ϵ_K , and the electrostatic repulsion of the surface proton by the cation immediately below the surface. The latter is taken as the ratio of the Pauling bond strength, s (= valence/radius) to the metal-oxygen bond length, $r_{\text{M-OH}}$ ($= r_{\text{M-O}} + 0.101$), hence:

$$\text{pH}_{\text{ppzc}} = -0.5 (\Delta\Omega_{\text{T}}/2.303RT) \cdot (1/\epsilon_K) - B(s/r_{\text{M-OH}}) + \log K_{\text{H}^+}^{\text{II}} \quad (10.15)$$

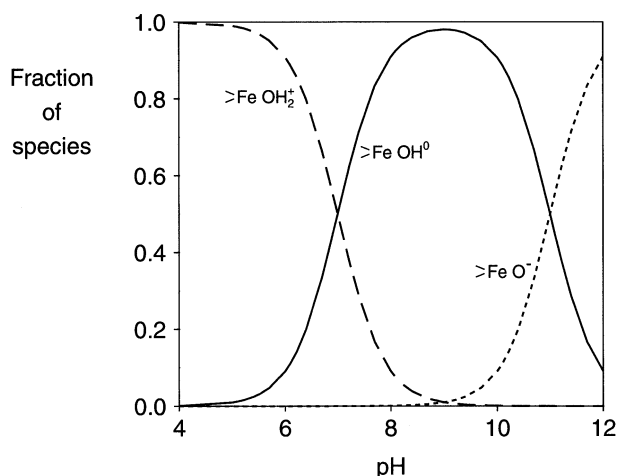


Fig. 10.7 Schematic representation of the distribution of positive, negative and neutral surface hydroxyl groups on an iron oxide surface with a $K_{\text{a1}}^{\text{s}} = 7.09$ and $K_{\text{a2}}^{\text{s}} = 11.11$.

(Ω_r = Born solvation term; B = coulombic repulsion term; $K_{H^+}^{II}$ = adsorption constant for H^+). An excellent correlation resulted between the experimentally determined and calculated pH_{pzc} for nine different solids, namely quartz, kaolinite, rutile, magnetite, goethite, hematite, corundum gibbsite and MgO. For the Fe oxides, the predicted (experimentally determined) values were: magnetite 7.1 (6.6), hematite 8.47 (8.5) and goethite 9.0 (9.4).

The values of the pzc/iep of iron oxides are influenced by several factors. The most important of these are the temperature and the presence of foreign ions in the system. The pzc of magnetite dropped from 6.5 to 5.4 as the temperature of the suspension was raised from 25 °C to 90 °C (Tewari and McClean, 1972). This may have been due, in part, to changes in the ionization constant of water as the temperature rose and also due to changes in the relative affinity of protons for the surface. Similarly, the pzc of hematite has been reported to fall as the temperature of the suspension rose (Lyklema, 1987). Dehydroxylation of the oxide and high temperature sintering reduces the number of surface hydroxyl groups and induces an acid shift in the pzc (Parks, 1965). Heating of hematite formed by wet precipitation, to a temperature above 1000 °C, caused the pzc to drop by three pH units (Penners and Koopal, 1986).

Specific adsorption of ions other than protons causes the pzc and the iep to shift along the pH scale (Stumm, 1992). Specifically adsorbed cations (anions) shift the titration curve and the point of zero proton condition at the surface ($pznpc$) to lower (higher) pH values, whereas the iep is moved to higher (lower) pH values. The shift of the iep of hematite to a lower pH by adsorbed EDTA and Cl^- is shown in Figure 10.8.

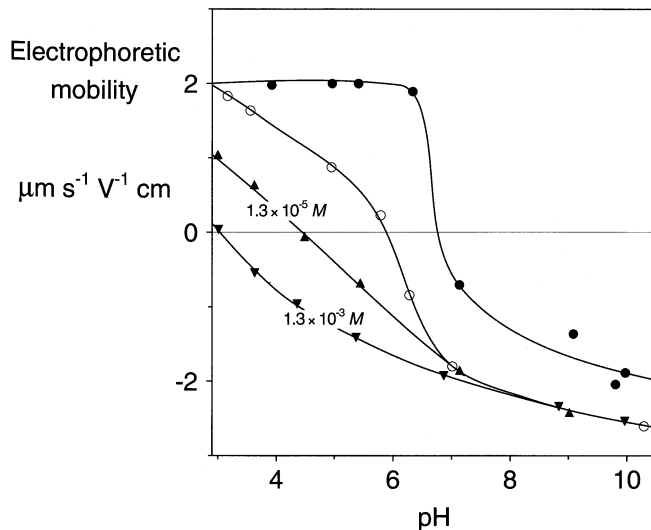


Fig. 10.8 Electrophoretic mobilities of spherical hematite particles in the absence and presence of EDTA ($1.3 \cdot 10^{-5}$ M, $1.3 \cdot 10^{-3}$ M) or chloride ions (o) vs. pH. o chloride contamination, ● chloride-free hematite (Matijevic, 1980, with permission).

Investigators tend to report either the pzc or the iep, but ideally, when specifically adsorbing ions are present, both parameters should be measured.

The pzc/iep is extremely sensitive to the presence of traces of impurities on the oxide surface. Low values have been obtained as a result of CO₂ species being adsorbed on the goethite surface (Lumsdon and Evans, 1994; Van Geen et al., 1994) and it is likely that most of the low values reported in the literature are due to CO₂ contamination. Shifts in the value of the pzc can indicate the presence of contaminants that are undetectable by conventional chemical analysis. Unpurged goethite, for example, had a pzc of 8.1 ± 0.1 , but two months of purging with N₂ raised the pzc to 9.0 ± 0.3 indicating that surface CO₂ had effectively been removed (Evans et al., 1979; Zeltner and Anderson, 1988). Hematite prepared from Fe^{III} chloride solution had an iep of 5.5 which, with extended washing in NaOH and hence, leaching of the chloride ions, moved to 7.2 (Hesleitner et al., 1987). Upon prolonged storage of this sample in water, the particle mobility and iep decreased owing to diffusion of chloride ions from the bulk of the oxide to the surface. Complete removal of the Cl⁻ by further washing again increased the particle mobility and raised the iep.

Iron oxides in soils and those used as pigments, are often associated with adsorbing species or with dopants such as phosphate, silicate and various metal ions; their iep's/pzc's will differ from those of the pure compounds. Soils rich in Fe oxides, therefore, have pzc's of 4–7, i.e. lower than those of pure iron oxides (see Chap. 16). The pzc of ferrihydrite coprecipitated with a small amount of silicate (with which it is often associated in nature) dropped from 7 to 5.3 (Schwertmann and Fechter, 1982; Anderson and Benjamin, 1985). Iron oxide properties are also modified by coating the particles with a different oxide. Coating hematite with silicate shifted the iep from 7 to 3 (Ohmori and Matijevic, 1992), whereas coating with aluminium or chromium oxide raised the iep (Garg and Matijevic, 1988). TEM examination of the spindle-shaped hematite particles showed that they were encased in a homogeneous, transparent Si coating the thickness of which was ca. 30 nm. Conversely, iron oxides adsorbed on negatively charged clay surfaces raised the pzc; upon removal of the oxides, the pzc fell (Escudey and Galindo, 1983). A biofilm of adsorbed bacteria (*Paenibacillus polymyxa*) on the surface of crystals of natural hematite lowered the iep of the Fe oxide from 5.8 to less than 2 (Deo et al., 2001).

The adsorption of humic material isolated from a eutrophic lake gave a synthetic goethite a negative charge over the pH range 4–8 (Fig. 10.9), thereby increasing the colloid stability and mobility of the oxide; this process also contributes to purification of natural waters (Tipping, 1981; Tipping and Cooke, 1982). Upon equilibration with lake water containing 1.6–2.1 mg L⁻¹ humics, goethite, hematite and ferrihydrite developed a negative charge down to pH 4. It was proposed that the large humic molecules displaced the electrokinetic shearplane to a distance from the oxide surface at which functional (carboxyl) groups determine the shear potential. At pH 3 fulvic acid reduced the zeta potential of hematite from 50 mV to -40 mV as the equilibrium concentration increased from zero to 10 mg L⁻¹; the zero potential (iep) occurred at ca. 0.5 mg L⁻¹ of humics. The charge neutralization led to the formation of compact hematite aggregates (TEM) with a fractal structure and a fractal dimension (see Chap. 5) obtained from the exponent of light scattering, of 2.58–2.93

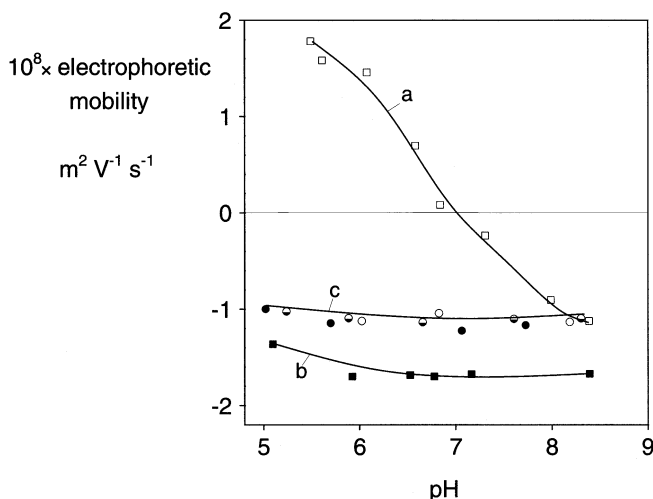


Fig. 10.9 Electrophoretic mobility of synthetic Fe oxides (0.01 g L^{-1}) in the presence of humic material from a eutrophic lake. Curve a: goethite in an $\text{Na}^+ \text{Cl}^- \text{HCO}_3^-$ medium, total ionic strength $2 \cdot 10^{-3} \text{ M}$, no humic material. Curve b: same as a but with 2.9 mg L^{-1} humic material. Curve c: goethite ($\square$), hematite ($\bullet$) and ferrihydrite ($\circ$) in the presence of lake water with 2.1 mg L^{-1} humic material (Tipping, 1981, with permission).

(Amal et al., 1992). A sample of dissolved organic matter from a swamp and also two weakly acidic, organic model compounds (polyaspartic and polyacrylic acid) induced a stable sol of hematite (60 nm particles) to form at pH 4.0 and 6.3, respectively (Tiller and O'Melia, 1993).

A permanent charge due to isomorphous substitution in the crystal structure as is found for layer silicates, does not contribute to the surface charge of pure Fe oxides. When, however, replacement of a proportion of Fe^{III} in the structure by another element occurs, a shift in the pzc would be expected unless the resulting negative charge surplus or deficit is compensated for by release or uptake of structural H, as happens for Fe^{III} substituted anatase (TiO_2) (Schwertmann et al., 1995) and Si substituted hematite (Campbell et al., 2002). A shift in pzc has been reported for Co-substituted magnetite. As the Co/Fe ratio in the surface layers of the magnetite particles increased from 0.1 to 0.5, the pzc of the ferrite shifted from 6.5 to 8.1, i.e. away from the value for magnetite (Ardizzone et al., 1987). Incorporation of Mn^{III} reduced the pzc of goethite slightly (Sun et al., 1999), whereas incorporation of up to $0.13 \text{ mol mol}^{-1} \text{ Cr}^{\text{III}}$ had no effect on the iep (Blesa et al., 1997).

10.5

Stability of Colloidal Suspensions

10.5.1

General

The stability of iron oxide suspensions is relevant to fields as varied as the paint industry, extraction of iron from its ores, the structure of soils, hydrometallurgy and waste water treatment. The ease of homogenisation of paint, for example, is controlled by proper adjustment of the stability of the pigment suspensions. In ground waters, the settling behaviour of small iron oxide particles influences transportation of trace elements and radio-nuclides. The stability of a dispersion of magnetic particles can determine the quality of ferrofluids and magnetic tapes.

The most widely used theory of suspension stability, the DLVO theory,¹⁾ was developed in the 1940s by Derjaguin and Landau (1941) in Russia and by Verwey and Overbeek (1948) in Holland. According to this theory, the stability of a suspension of fine particles depends upon the total energy of interaction, V_T , between the particles. V_T has two components, the repulsive, electrostatic potential energy, V_R , and the attractive force, V_A , i.e.

$$V_T = V_R + V_A \quad (10.16)$$

The repulsive force depends on the double layer potential and thickness, the particle radius and the dielectric constant of the medium, whereas the attractive force arises from retarded London/van der Waals forces.

The potential energy curve, a plot of V_T versus distance from the surface has three features; the energy barrier and two minima. The shape of the curve, in particular, the height of the barrier and the depth of the secondary minimum, depends on the magnitude of the interacting forces. Attraction decreases inversely with the sixth power of the distance between the particles and predominates at very large and very small separations, except at distances of the order of atomic dimensions where repulsion takes place. Repulsion varies exponentially with distance and, if large enough, may predominate at intermediate distances, in which case a potential energy barrier develops. This barrier must be surmounted before the particles can coagulate in the primary minimum.

The magnitude of the repulsive force and hence the height of the energy barrier depends on the four factors mentioned above. The thicker the double layer around the particles, the greater the repulsion between them and the greater the stability of the suspension. The double layer thickness may range from a few nm at high ionic strength to several tens of nm at low ionic strength. Increasing the concentration of inert electrolyte in the system compresses the double layer, reduces the height of the potential energy barrier and promotes coagulation. The effect of the inert electrolyte

1) An alternative theory originally proposed by Langmuir (1938) is discussed in the article by McBride (1997).

depends principally on the concentration and valency of the counter ion and increases as these parameters rise (Schulze/Hardy rule). The critical coagulation concentration (CCC) is the minimum concentration of electrolyte required to reduce the potential energy barrier to zero so that the particles coagulate and sediment under gravity. Flocculation of an aqueous suspension is also induced by addition of a water miscible, organic solvent. This reduces the dielectric constant of the medium and so compresses the electrical double layer around the particles. An example of this is the addition of paratoluene sulphonate to precipitate the polymers formed during the initial stages of hydrolysis of FeCl_3 solution so that the structure could be examined by XRD (Schneider and Schwyn, 1987). In both water and organic solvents to which an inert electrolyte is added, coagulation by monovalent counter ions is due to compression of the double layer. Bi- and multivalent ions, however, cause coagulation in polar organic solvents by a charge neutralization mechanism (de Rooy et al., 1980). The slow coagulation of small ($40 \cdot 100$ nm) acicular goethite crystals at low pH is considered to be facilitated by the parallel alignment of crystals within an aggregate (Van der Woude et al., 1984a).

If the potential energy barrier is high compared with the thermal energy, kT , (k is the Boltzman constant and T the absolute temperature) of the particles, the suspension will be stable. In general a barrier of $> 25 kT$ is sufficient to stabilize a suspension indefinitely. This corresponds to a zeta potential of greater than 30 mV. Even when the barrier is high enough to prevent the particles from moving into the primary minimum, they may still be trapped in the secondary minimum (flocculation) if this is deep compared with the thermal energy of the particles. As the secondary minimum is often shallow ($< kT$), flocculation is readily reversible.

For oxides such as magnetite, maghemite and even hematite, magnetic interactions may affect the stability of the suspension. Cubic particles, $1.2 \mu\text{m}$ across of hematite, which is weakly magnetic, formed loose chains at low ionic strength with each particle being at some distance from its neighbour (Ozaki and Matijevic, 1988). Chain formation was attributed to attractive van der Waals forces enhanced by a contribution from weak magnetic forces which lead to flocculation into the secondary minimum. This flocculation could be readily reversed by stirring the suspension or by altering the orientation of the magnetic field. This topic is discussed in detail in Matijevic (2000).

Repulsive forces between Fe oxide particles can be established by adsorption of suitable polymers such as proteins (Johnson and Matijevic, 1992), starches, non-ionic detergents and polyelectrolytes. Adsorption of such polymers stabilizes the particles at electrolyte concentrations otherwise high enough for coagulation to occur. Such stabilization is termed protective action or steric stabilization. It arises when particles approach each other closely enough for repulsive forces to develop. This repulsion has two sources. 1) The volume restriction effect where the ends of the polymer chains interpenetrate as the particles approach and lose some of their available conformations. This leads to a decrease in the free energy of the system which may be sufficient to produce a large repulsive force between particles. 2) The osmotic effect where the polymer chains from two particles overlap and produce a repulsion which prevents closer approach of the particles.

The rate of coagulation depends on the height of the potential energy barrier. In the absence of a barrier, the rate of disappearance of the primary particles is controlled by the number of collisions between particles, i.e.

$$\frac{dn}{dt} = k_0 n^2 = 8\pi DRn^2 \quad (10.17)$$

where n = the number of particles per unit volume present initially, D is the diffusion coefficient, R is the collision radius and k_0 is a constant. A potential energy barrier retards coagulation and, in its presence, the rate becomes,

$$\frac{dn}{dt} = \frac{k_0 n^2}{W} \quad (10.18)$$

W is the stability ratio, i.e. the factor by which the coagulation velocity is reduced due to interparticle repulsion. It is related to the height of the energy barrier. When coagulation is fast, $W = 1$. Various aspects of slow coagulation are still not fully understood (O'Melia, 1987). Several theories of the kinetics of coagulation are discussed by Grand et al. (2001).

10.5.2

Stability of Iron Oxide Suspensions

The stability of iron oxide suspensions is often monitored using light scattering/turbidity measurement (Figure 10.10). Monodisperse samples of spherical hematite are well suited to this type of investigation. Fast coagulation takes place at the pzc/iep and also at the extremes of pH where the ionic strength is high (Fig. 10.10).

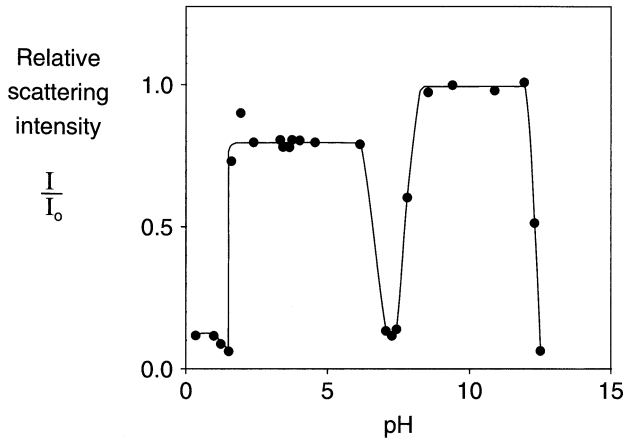


Fig. 10.10 Relative scattering intensity as a function of pH of a hematite sol with a pzc of 7. High I/I_0 values represent stable sols (Matijevic, 1980, with permission).

This property is utilized when washing and filtering freshly precipitated iron oxides by adjusting the pH of the suspension and that of the washing medium to that of the pzc, so that salts may be readily washed out of the solid. At pH 5 and low ionic strength, coagulation of hematite is one thousandfold slower than at the pzc. Coagulation of isodimensional hematite particles (ca. 50 nm in size) with KCl at pH 3, led to aggregates with fractal dimensions of 2.3 for rapid and 2.8 for slow coagulation (Amal et al., 1990). At low temperatures and low salt concentrations, hematite particles coagulate slowly to form tightly packed, compact structures, whereas rapid coagulation leads to loose aggregates (Amal et al., 1990a). The settling of colloids can also be followed by microscopy and by Small Angle X-ray Scattering (SAXS). With the latter technique, various maxima corresponding to diameters ranging from one to seven nm were found for ferrihydrite agglomerates (Bottero et al., 1991; Tchoubar et al., 1991).

Adsorption of ions modifies the charge properties of Fe oxides and hence affects the stability of the suspension. Adsorption of sufficient amounts of the tungstosilicate ion, $\text{SiW}_{12}\text{O}_{40}^{4-}$, to just neutralise the positive surface charge caused hematite to coagulate over the pH range 3–6. Higher levels ($> 5 \cdot 10^{-8}$ M) of this ion, restabilised the suspension because the extent of adsorption had now increased sufficiently to produce a negative charge on the surface, i.e. charge reversal had occurred (Matijević, 1980). Other adsorbing anions such as phosphate, pthallate, citrate, long chain carboxylic acids and fulvic and humic acids had a similar stabilising/destabilising effect as their concentration in the system was varied (Van der Woude et al., 1986; Liang et al., 1988). The hematite/water interface is a *structure promoter*¹⁾ (MacCafferty and Zettlemoyer, 1971) and so, preferentially adsorbs structure making ions such as Na^+ and Li^+ (above the pzc) and IO_3^- and F^- (below the pzc). In the presence of a *structure breaking* species such as urea, the structure making ability of the surface and any associated ions is reduced (Amhanmdi et al., 1997). Figure 10.11 illustrates the coagulation of hematite in the presence of KNO_3 , K_2SO_4 (Fig. 10.11 upper) and phosphate (Fig. 10.11 lower). Close to the pzc (ca. 8.5 in KNO_3 and 9.6 in K_2SO_4), very low salt concentrations were needed to coagulate hematite. The phosphated hematite formed a stable (positive) sol at much lower concentrations of sodium phosphate in the acid range than in the alkaline range where the sol is negatively charged. Phosphate has a strong stabilising effect over a wider concentration range than does KNO_3 or K_2SO_4 . The different domains of stability/settling in the concentration vs. pH diagram have been attributed to charge reversal due to adsorption of different species: at pH < 8 , for example, stabilisation by low levels of phosphate is attributed to adsorption of HPO_4^- (Breeuwsma, 1971).

Low to medium amounts of sodium dodecyl sulphate and sulphonate make hematite hydrophobic and cause coagulation, but with higher levels of these *surfactants*, hematite again becomes hydrophilic and is redispersed (Fuerstenau and Colic,

1) Each water molecule can form hydrogen bonds with four neighbours with the result that a three dimensional network of molecules, i.e. a structure, is established. This structure can be modified by solute molecules

and also by charged interfaces. Structure breakers are solutes that increase the randomness of water (compared with that of the bulk water); structure makers have the reverse effect.

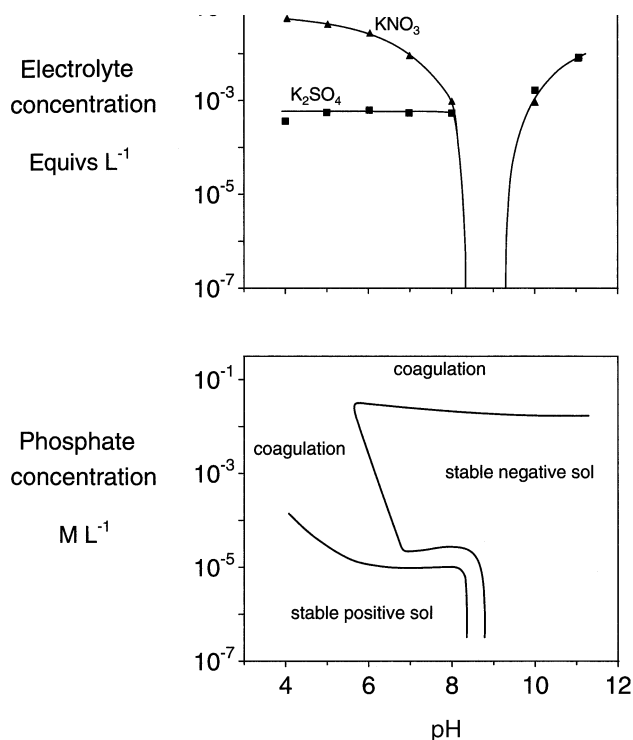


Fig. 10.11 Stability regions of a hematite sol as a function of pH. Top: in the presence of KNO₃ and K₂SO₄. The sol is stable in the region under the curves; bottom: in the presence of phosphate (Breeuwsma, 1973, with permission).

1999). The surfactants associate at the oxide surface to form hemi-micelles with their hydrophobic groups exposed to the aqueous phase at low concentrations, but at higher concentrations, with the hydrophilic groups turned outwards. Hematite coated with various proteins (ovalbumin, γ -globulin, lysozyme) adopted either the iep of the proteins or a value between that of the oxide and the protein and displayed modified coagulation behaviour (Johnson and Matijevic, 1992).

Charge reversal effects have also been reported for goethite. At close to neutral pH (6–6.5), coagulation was induced by much lower levels of NaCl or KCl than by CaCl₂ or AlCl₃; the latter electrolytes strongly favoured dispersion of goethite (Ramos and McBride, 1996). This behaviour was attributed to chemisorption (see Chap. 11) of Al species and, to a lesser extent, of Ca species, on the goethite. Low levels of organics – citrate, salicylate and humics –, promoted coagulation in slightly acidic media, but high levels redispersed the goethite particles. Soluble aluminium species and also calcium ions counteracted the effects of high levels of humics and promoted coagulation. These effects were again attributed to reversal of the surface charge (Ramos and McBride, 1996).

The absolute values of the settling rate constant for hematite as a function of pH and ionic strength were measured using both static and dynamic light scattering (Schudel et al., 1997). At high ionic strength, the settling rate was independent of pH and had values of $1\text{--}4 \cdot 10^{-18} \text{ m}^3 \text{ sec}^{-1}$, which is around an order of magnitude lower than the value found by single particle counting (Lichtenfeld et al., 1995): an explanation for the discrepancy is not yet available. The rate of settling as a function of pH, was asymmetric around the pzc, being much less pH dependent at lower pHs. The authors suggested that the interaction forces differ in the two pH regions, but Hiemstra and Van Riemsdijk (1999) proposed that, at least for platy crystals, the asymmetry is due to the predominance of the mainly uncharged (001) plane of hematite. Only part of the settling data fitted predictions by the DLVO theory. Polyacrylic acids caused hematite particles to coagulate with the maximum settling rate being the same as that found in a simple electrolyte (Ferreti et al., 1997). This result suggested that, at least in this system, polymer induced coagulation was due more to charge neutralisation than to bridging by polymers.

Although high levels of adsorbed polymers stabilize particles, low levels of the same polymer may induce coagulation by bridging particles, thereby forming large flocs. Starch (2.5 kg^{-1}), for example, is used as a flocculant to separate the red muds (a mixture of goethite and hematite) from the sodium aluminate solution obtained by extraction of bauxite (Yamada et al., 1980). Another example of this is the use of selective flocculants in mineral processing to separate small ($< 10 \text{ nm}$) particles of hematite ore from silica and thus assist their recovery. This process (the Tilden process) was first introduced at the Tilden iron ore mine in the USA (Villar and Dawe, 1975). The ore is dispersed in sodium silicate solution to increase the surface charge and corn starch, which selectively flocculates the hematite, is then added. The mechanism of interaction has not been fully established but it is thought that hydrogen bonding between the hydroxyl groups of the starch and those on the mineral surface is involved. Although the individual linkages are weak, there are so many of them that the total bonding energy is large (Iwasaki, 1978). The greatest probability of successful floc formation occurs with about half the concentration of flocculant that is required to reach saturation density. A recent development in this field is the use of bioflocculants (e.g. yeasts) to flocculate hematite (Smith et al., 1994).

One area in which steric stabilisation of iron oxides is important is that of ferrofluids (see Chap. 19). To avoid settling of the magnetic particles, stabilisation against coagulation is effected either electrostatically or by means of surfactants (Gornert and Buske, 2000 and references therein). The radius of the magnetic core can be up to 4.4 nm and that of the surfactant shell around 1.8 nm (Karmel et al., 2001). An even more effective stabilisation technique involves coating magnetite with SiO_2 to lower the pzc followed by adsorption of an organic coating (Philipse et al., 1994). Another method makes use of double layers of surfactant with the particles being coated with primary and secondary layers composed of different fatty acids (Wooding et al., 1992). The concentration dependence of the sedimentation rate of magnetite particles coated with various nonmagnetic shells (SiO_2 or surfactant layers) is strongly affected by the thickness of the non magnetic shell (Donseelaar et al., 1997).

The stability of a mixture of magnetite and cobalt ferrite particles as a function of pH and magnetic field strength was followed with turbidity measurements (de Vincente et al., 2000). In the presence of a magnetic field and at particle concentrations above 0.7 gL^{-1} , the stability of the suspension rose as the magnetic field increased. Potential energy calculations which took magnetic dipole interactions into account showed, however, that the potential barrier between the particles fell as the magnetic field became greater. A possible explanation for the discrepancy may be that, as the particles form chains in the presence of a magnetic field, the potential energy effect was counteracted by the long range structure which helped stabilise the system as the magnetic field was increased.

In addition to coagulation with each other, particles of iron oxide can coagulate with other substrates of different size and charge (heterocoagulation). In acid media of low ionic strength, heterocoagulation of small (10 nm) negative particles of gold with large (several nm) particles of positively charged goethite occurs. The process is dominated by electrostatic effects (Enzweiler and Joekes, 1992). This type of heterocoagulation was promoted by raising the temperature of the system (from 0 to 42°C), whereas desorption of gold was induced by raising the pH above 6. As gold is often associated with iron ores in laterites, this type of interaction is relevant to geochemistry.

Another example of heterocoagulation is shown in Figure 10.12. Increasing amounts of goethite added to kaolinite significantly raised the pH of the iep of the latter material from below 2 to above 6, i.e. towards the iep of pure goethite. This suggests that there was a close association between the two phases leading to a gradual conversion from negatively charged to positively charged surfaces. No separate migration of goethite and kaolinite during electrophoresis was observed (Venema & Glasauer, unpubl.).

Similarly, the pH at zero zeta potential in three lateritic soil materials consisting essentially of serpentine and goethite moved from 5.1 to 6.0 and to 8.2 as the goethite percentage increased from 50 to 79 and to 91% (Cerpa et al., 1999). Both results suggest that there was a close association between the clay silicate and goethite leading to a gradual conversion from negatively charged to positively charged surfaces.

The colloidal behaviour of iron oxides is of great importance in the environment. A large range of unwanted chemicals, especially in soils and sediments may be transported with the moving water in porous substrates “at the back” of iron oxides. The stability of nano-sized Fe oxide particles can be modified by these sorbates. As an example, the colloidal stability of 122nm-sized monodispersed hematite crystals, as measured by the collision efficiency in a sand column, increased 100fold through the adsorption of a soil humic acid which reversed their charge from positive to negative (Kretschmar and Sticher, 1997). The effect of various carboxylic polymers at various concentrations on the suspension stability of tens-nm-sized hematite went through a minimum probably due to a charge reversal. This was shown both for synthetic (e.g. polyacrylic acid; Zhang and Buffle, 1995 and polyaspartic acid; Liang and Morgan, 1990) and for natural ones (fulvic acid from Suwannee River; Tipping and Higgins, 1982; and humic acid; Liang and Morgan, 1990).

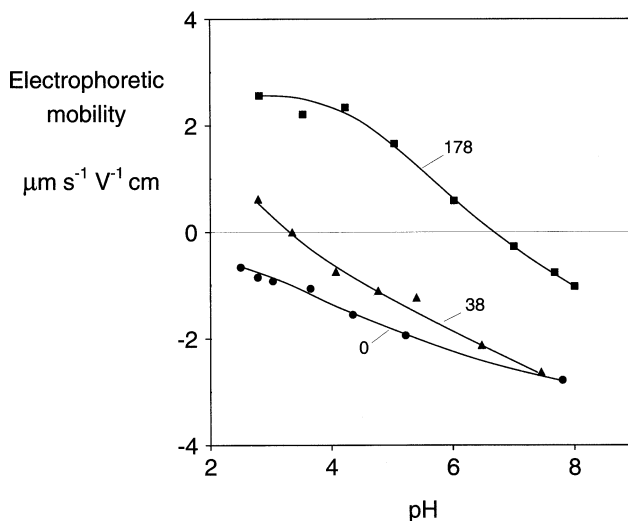


Fig. 10.12 The effect of increasing amounts of goethite (surface area $51 \text{ m}^2 \text{ g}^{-1}$) on the electrophoretic mobility of kaolinite at various pH. The figures on the curves indicate the amount of goethite added (mg g^{-1}) (Venema and Glasauer, unpubl.).

The cationic surfactant hexadecyltrimethylammonium bromide (HDTMA) induced dispersion of goethite in a column of material from a surface soil and a aquifer substrate, possibly because the HDTMA reduced the negative charge of the clay particles and thereby desorbed the goethite (Seaman and Bertsch, 2000).

A special case of heterocoagulation is the adhesion of particles to substrates. Investigation of the deposition of iron oxides on, and the desorption from various substrates is relevant to corrosion and cleaning processes. Deposition of hematite particles ($< 1 \text{ } \mu\text{m}$) on glass beads ($50\text{--}100 \text{ } \mu\text{m}$) packed in a column involves a multilayer adhesion process (Matijevic, 1980). The extent of adhesion is strongly affected by ionic strength and depends on the collision efficiency of the particles with respect to the unoccupied and the already covered surface and also on the maximum concentration possible in a monolayer (Ryde et al., 1992). Quantitative adsorption of hematite on steel occurs in the pH range over which the two materials are oppositely charged, with an adsorption maximum at pH 6.7 (Fig. 10.13). Again, electrostatic forces are involved. Desorption of hematite from the steel substrate could be partially described in terms of potential energy interactions. In addition, particles were trapped in crevices on the steel surface and these could not be desorbed (Kuo and Matijevic, 1980). Adhesion of hematite to the steel could be enhanced by the application of a magnetic field which promoted deposition of the particles into a deep secondary minimum. Such particles were readily detached once the magnetic field was removed. Adsorption of hematite onto silver and mercury electrodes has been reported (Andrade et al., 1994, 1994a) and also adsorption of small, polystyrene latex particles on larger hematite crystals (Hansen and Matijevic, 1980). Deposition of

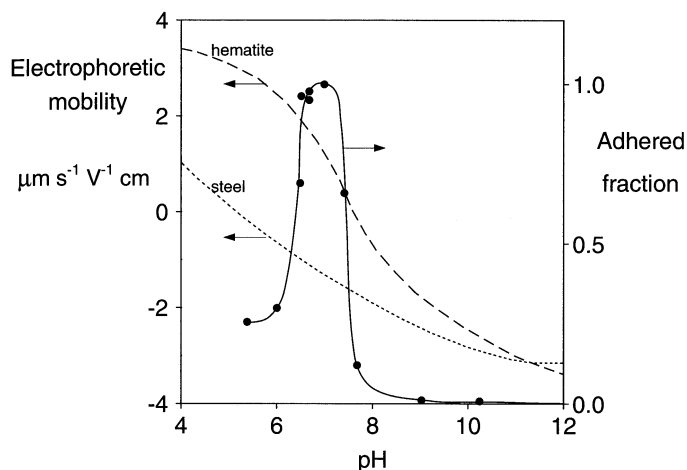


Fig. 10.13 Fraction of hematite particles deposited on steel as a function of pH at 25°C (solid line). For each point 50 cm³ of the hematite sol ($d_{\text{modal}} = 170 \text{ nm}$ and $10^8 \text{ particles cm}^{-3}$) was passed through the bed at a flow rate of one cm³ min⁻¹. Dashed lines represent the electrophoretic mobilities of the hematite and of the steel particles (Matijevic, 1980, with permission).

hematite on glass in the presence of 4 octylbenzene sulphonate (NaOBS) changed from monolayer to multilayer as the concentration of the surfactant in the system increased (Zelenev and Matijevic, 1997). Adsorption of SiO₂ particles onto glass beads was promoted by the presence of hematite particles. A bridging mechanism in which the positively charged hematite linked the negatively charged oxide particles and the beads, operated. Desorption of both types of oxide from the glass was effected by raising the pH of the system to above 9 (Mendoza et al., 1996, 1996a).

SiO₂ sand has been coated with various well defined Fe oxides and used as a model system for studying adsorption and dissolution with the Fe oxide being in a mechanically stable form. Cristobalite sand coated with goethite has been used as the matrix in column experiments to study the reactive transport behaviour of protons (Scheidegger et al., 1994; Burgisser et al., 1994), fluoride (Meeussen et al., 1996), sulphate (Meeussen et al., 1999), phosphate (Geelhoed et al., 1997) and uranyl ions (Gabriel et al., 1998). Transport studies of the movement of fairly monodisperse crystals (0.12 μm in length) of goethite through a quartz packed column showed that at low pH, the goethite was strongly retained by the quartz (Sätmark et al., 1994). Mobilisation of natural colloids in a (presumably) ferrihydrite coated aquifer sediment increased with rising pH until the simultaneous increase in ionic strength limited further release of the particles (Bunn et al., 2002).

10.6

Tactoids, Gels and Schiller Layers

Tactoid formation and gelation are evidence of the operation of long range forces in colloidal suspensions. Tactoids are spindle shaped droplets in which there is a higher density of crystals than in the surrounding medium; concentrated suspensions of akaganéite can form tactoids (Mackay, 1962). Where the attractive forces between particles in a concentrated suspension are strong enough a gel, i.e. a continuous aggregate, may form. A very stable, viscous gel was induced to form in a concentrated suspension of an acicular “Fe oxyhydroxide” (not identified, but probably akaganéite): the particles sedimented when the electrolyte concentration was increased (Zringi et al., 1993).

When a concentrated suspension of fairly monodispersed crystals of akaganéite is allowed to settle over a few months, a thick sediment, the lower part of which displays brilliant interference colours, forms (Zocher, 1925; Zocher and Heller, 1930). These colours indicate the existence in the sediment of ordered structures termed schiller layers (from the German word for iridescence). These schiller layers consist of mats of aligned crystals of β -FeOOH with the mats being stacked perpendicular to the direction in which the crystals are aligned. Formation of these structures is considered to be the result of a phase separation (similar to that observed in some monodisperse latices) which leads to a concentrated, ordered phase, the sediment, separating out and coexisting with the suspension (the disordered phase) (Maeda and Hachisu, 1983). AFM examination of the dried sediment showed that it contains regions with different orientations (Maeda and Maeda, 1996). The ordered regions that were responsible for the iridescence consisted of square lattices of upright crystals (vertical layers), whereas in the greyish, non iridescent regions, the crystals were randomly oriented, or lay parallel in horizontal layers (Fig. 10.14). The colours (Plate 10.1) are attributed to interference of visible light caused by the spatial periodicity (close to the wavelength of visible light) of the layers composed of the vertically aligned crystals.

10.7

Rheological Properties

The flow behaviour or rheology of suspensions under the influence of external mechanical forces has important theoretical and industrial applications. For Fe oxides, rheological properties influence, among other things, the properties of paints and magnetic recording tapes. Recent texts on rheology include those by Goodwin and Hughes (2000) and Barnes (2000). In this section, some important definitions are listed: other details are found in the above texts.

When a shear stress is applied to a suspension or liquid exhibiting laminar flow, a velocity gradient (the *rate of shear*) is established. When the rate of shear varies linearly with the applied shear stress, the system is termed Newtonian and the proportionality constant is termed the *viscosity*. Newtonian flow is usually observed in dilute

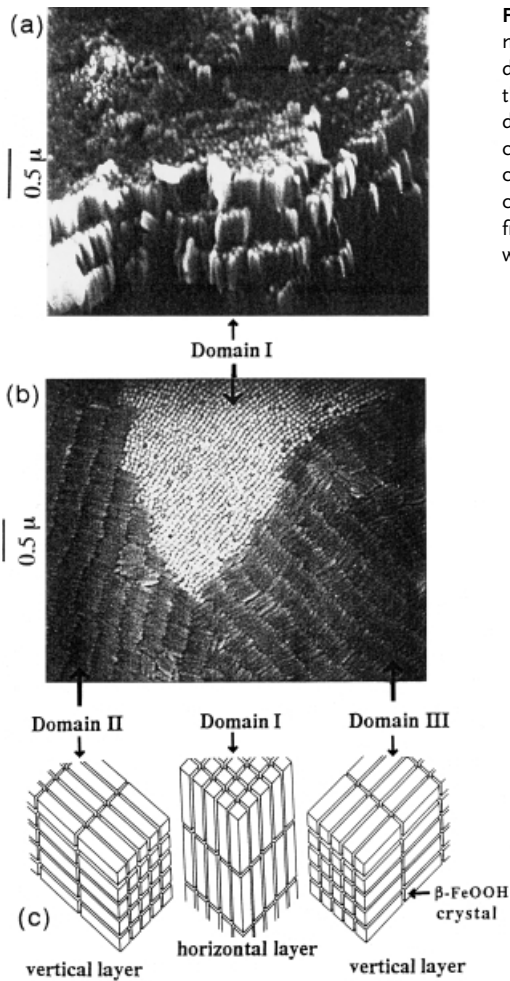


Fig. 10.14 a) SEM of three smectic domains I, II and III of β -FeOOH crystals. In domain I the crystals stand upright so that only the ends are visible, whereas in domains II and III, only the sides of the crystals are visible. b) SEM of domain I. c) Schematic figure of the arrangement of crystals in the three domains (Reprinted from Maeda & Maeda, copyright 1996, with permission and Courtesy, H. Maeda).

suspensions. In systems with non Newtonian behaviour, the value of the viscosity at any point depends upon the rate of shear, hence an apparent viscosity is measured. One example of non Newtonian flow is *plastic flow*, where (observed) flow only occurs when the applied stress is above a certain limiting value termed the *yield stress*, τ . As a suspension is coagulated at the pH of the iep, the yield stress is at a maximum at this pH: it is a measure of the strength of the floc structure. Where the suspension is concentrated enough to form a gel, *thixotropic* behaviour may be observed, i.e. the particle network breaks down upon stirring and the suspension flows: upon rest, however, the gel reforms.

The rheological properties of a suspension depend upon factors such as the size, shape and concentration of the particles, the stability of the suspension and the viscosity of the medium. Flow properties can be modified by altering the surface charge

on the particles and these, in turn, can be changed by varying the pH and ionic strength of the system.

Rheological studies involving Fe oxides appear to be sparse. Most are carried out on acicular crystals, usually maghemite. Details of the method of synthesis or properties of the particles are often lacking.

A detailed study was made over a wide range of concentrations and shear rates of the intrinsic viscosity and other rheological properties of acicular maghemite and both acicular and rhombohedral hematite particles in ethylene glycol (Smith and Bruce, 1979). Garcell et al. (1998) compared the behaviour of three samples of maghemite with surface areas ranging from 26–65 m² g⁻¹ and noted that the maximum yield stress at a fixed solids concentration, decreased as the average particle size decreased. This unexpected behaviour was attributed to the superparamagnetic behaviour of the sample with the smallest particles (12 nm). A floc network model for Fe oxides has been developed by Kanai et al. (1992).

Cryogenic scanning microscopic examination of flocs of “needle-like” Fe oxide in mineral oil provided information about how flocs break up when subjected to different rates of flow (Navrette et al., 1996). The suspensions exhibited strong yielding behaviour, i.e. the viscosity fell dramatically over a narrow range of stress particularly at volume fractions greater than 6%. After yielding, the suspensions underwent shear thinning, i.e. the viscosity fell as the rate of shear rose.

Cerpa et al. (1999) found a relationship between the yield stress and the volume fraction of a laterite suspension consisting of serpentine (a clay mineral) and goethite.

11

Adsorption of Ions and Molecules

11.1

General

The adsorption of ions on iron oxides regulates the mobility of species in various parts of the ecosystem (biota, soils, rivers, lakes, oceans) and thereby their transport between these parts. Examples are the uptake of plant nutrients from soil and the movement of pesticides and other pollutants from soils into aquatic systems. In such environments various ions often compete with each other for adsorption sites. Adsorption is the essential precursor of metal substitution (see Chap. 3), dissolution reactions (see Chap. 12) and many interconversions (see Chap. 14). It also has a role in the synthesis of iron oxides and in crystal growth. In industry, adsorption on iron oxides is of relevance to flotation processes, water pollution control and waste and anticorrosion treatments.

The adsorption process involves interaction of the adsorbing species, the *adsorbate*, with the surface hydroxyl groups on the iron oxide, the *adsorbent*. The oxygen donor atom of the surface hydroxyl group can interact with protons (see Chap. 10), whereas the underlying metal ion acts as a Lewis acid and exchanges the OH group for other ligands to form surface complexes.

Studies of adsorption on iron oxides have followed two main lines:

1. Measurement of the extent to which the adsorbent removes the adsorbate from a liquid or gaseous phase. The data is used to construct adsorption isotherms and is often fitted to a model to provide information about binding constants, adsorption maxima and other parameters, and also speciation of surface complexes. Kinetic data may also be obtained.
2. Spectroscopic investigations to determine the structure of the surface complexes formed through adsorption and to help distinguish between adsorption of metals and their surface precipitation. Various surface-specific spectroscopic techniques are now used for this purpose, in particular IR, XPS, EPR and XAS (see Chap. 7). For reviews see Brown (1990), Manceau et al. (1992), Brown et al. (1995) and Blesa et al. (2000).

The so called “hydrous ferric oxide, HFO”, i. e. 2-line ferrihydrite, has been a classic sorbent for all kinds of adsorption studies (see Jambor and Dutrizac, 1998) and Dzombak and Morel (1990) have devoted a whole book to the results of these studies.

Equally often, goethite and hematite have been used as model adsorbents because they have a well defined crystal structure, are widespread in nature and can be synthesized readily in the laboratory.

11.2

Treatment of adsorption data

Adsorption data are frequently presented as a plot of the amount of adsorbate taken up per unit weight or area of the adsorbent vs the equilibrium concentration remaining in the gaseous or solution phase (adsorption isotherm); pH, temperature and electrolyte concentration are held constant. Depending upon the purpose of the investigation, the extent of adsorption is expressed either as amount of adsorbate vs. surface area of adsorbent, as fraction adsorbed, or, in some cases, as a distribution coefficient, K_d .

The adsorption data is often fitted to an adsorption isotherm equation. Two of the most widely used are the Langmuir and the Freundlich equations. These are useful for summarizing adsorption data and for comparison purposes. They may enable limited predictions of adsorption behaviour under conditions other than those of the actual experiment to be made, but they provide no information about the mechanism of adsorption nor the speciation of the surface complexes. More information is available from the various surface complexation models that have been developed in recent years. These models represent adsorption in terms of interaction of the adsorbate with the surface OH groups of the adsorbent oxide (see Chap. 10) and can describe the location of the adsorbed species in the electrical double layer.

11.2.1

The Langmuir, Freundlich and Temkin isotherm equations

The *Langmuir* equation applies to a reaction of a surface Fe ($\equiv\text{Fe}$) atom with an adsorbate molecule X, e. g.,



The equilibrium constant K_{ads} is then:

$$K_{\text{ads}} = \frac{[\equiv\text{FeX}]}{[\equiv\text{Fe}][\text{X}]} \cdot \exp \frac{(-\Delta G_{\text{ads}})}{RT} \quad (11.2)$$

with $-\Delta G_{\text{ads}}$ being the free energy of adsorption.

The Langmuir equation is written as

$$\Gamma_{\text{X}} = \Gamma_{\text{max}} \left(\frac{K_{\text{ads}} \cdot X_{\text{aq}}}{1 + K_{\text{ads}} \cdot X_{\text{aq}}} \right) \quad (11.3)$$

where X_{aq} is the equilibrium concentration (or pressure for a gas) of the adsorbate and Γ_X = mass adsorbate/mass adsorbent. Γ_{max} corresponds to the level of adsorbate required to saturate all available surface sites (at $X_{aq} \gg 1$) and provide a monolayer coverage. This equation relates the amount adsorbed to the equilibrium concentration, X_{aq} , of the adsorbate in the bulk solution. Overall, adsorption increases with rising adsorbate concentration until a plateau corresponding to saturation of all surface sites is reached. The relative adsorption, however, decreases with rising adsorbate concentration. The initial slope of the isotherm K_{ads} , the equilibrium adsorption constant, is a measure of the affinity of the adsorbate for the adsorbent. From a linearized form of this equation; i. e.

$$\frac{1}{\Gamma_X} = \frac{1}{\Gamma_{max}} + \frac{1}{K_{ads} \cdot \Gamma_{max} \cdot X_{aq}} \quad (11.4)$$

K_{ads} and the saturation adsorption may be evaluated.

Anion adsorption on iron oxides is frequently described by this equation whereas cation adsorption data is often fitted to the *Freundlich* equation, i. e.

$$\Gamma_X = K_{ads} X_{aq}^{1/n} \quad (11.5)$$

Although this equation is very convenient for representing data, it is purely empirical; n is an adjustable parameter that characterizes the adsorption affinity. The effect of adsorbent concentration on the extent of adsorption has been treated by McKinley and Jenne (1991).

Whereas the Langmuir equation assumes a uniform energy of adsorption, the *Temkin* equation uses a logarithmic relationship

$$\Gamma_X = A \ln X_{aq} \quad (11.6)$$

thereby taking into account the heterogenous surface on which the adsorption energy decreases as the coverage increases.

11.2.2

Surface complexation models

The surface complexation models differ from the above equations in that they explicitly define the chemical reaction involved in the adsorption process. A crucial feature of these models is the treatment of adsorption as an interaction of adsorbing species with well defined coordination sites (the surface OH groups) in a manner analogous to complexation reactions in solution. A further feature of these models is that the chemical free energy of adsorption predominates with electrostatic effects having but a secondary role.

These models describe the development of surface charge and potential together with ion adsorption in a quantitative manner. They have in common a set of simultaneous equations that can be solved by numerical methods using the appropriate

values for such parameters as the number of surface sites, the binding constants and the double layer capacitance(s). There are four sets of equations:

1. The mass action equation for the surface reaction.
2. The mass balance equation for the surface OH groups.
3. Equations for the calculation of surface charge.
4. Equations that describe the relationship between the charge and the potential of the electrical double layer.

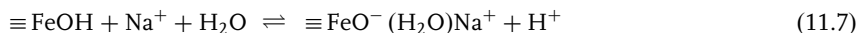
The main, currently used, surface complexation models (SCMs) are the constant capacitance, the diffuse double layer (DDL) or two layer, the triple layer, the four layer and the CD-MUSIC models. These models differ mainly in their descriptions of the electrical double layer at the oxide/solution interface and, in particular, in the locations of the various adsorbing species. As a result, the electrostatic equations which are used to relate surface potential to surface charge, i.e. the way the free energy of adsorption is divided into its chemical and electrostatic components, are different for each model. A further difference is the method by which the weakly bound (non specifically adsorbing; see below) ions are treated. The CD-MUSIC model differs from all the others in that it attempts to take into account the nature and arrangement of the surface functional groups of the adsorbent. These models, which are fully described in a number of reviews (Westall and Hohl, 1980; Westall, 1986, 1987; James and Parks, 1982; Sparks, 1986; Schindler and Stumm, 1987; Davis and Kent, 1990; Hiemstra and Van Riemsdijk, 1996; Venema et al., 1996) are summarised here.

The constant capacitance model was developed by the groups of Schindler and Stumm in Switzerland in the early 1970s (Schindler and Kamber, 1968; Hohl and Stumm, 1976). It is a special case of the DDL model developed for systems at (comparatively) high ionic strength. The electrical double layer is treated as a parallel plate capacitor, i.e. it is based on the Helmholtz model (see Chap. 10). All the adsorbing ions are located in one plane and thus experience the same potential. Examples of the application of the model include the adsorption on goethite of phosphate and silicate (Sigg and Stumm, 1981), polyphosphonates (Nowack and Stone, 1999) and mixtures of anions (Goldberg, 1985; Manning and Goldberg, 1996) and the adsorption of phosphate in soils (Goldberg and Sposito, 1984).

The diffuse double layer model is based on the Gouy Chapman model and was developed by Stumm et al. (1970). The potential determining and specifically adsorbing ions are located in the plane at the surface with the counter ions being in the diffuse layer. This model, which considers there to be a fixed number of surface sites, is applicable over a range of ionic strengths. It was later modified to incorporate strong and weak adsorption sites (and termed the generalised Two Layer Model) and used as such by Dzombak and Morel (1990) to provide a self consistent data set for cation and anion adsorption on ferrihydrite. In this form it has been used to model adsorption on goethite of simple aromatic acids (Evanko and Dzombak, 1999) and Cu and Ca (Ali and Dzombak, 1996b) and the adsorption of Yb and Ni on magnetite (Marmier et al., 1999).

In the triple layer model, the potential determining ions are located at the oxide surface with the specifically adsorbing ions and the ion pairs in the inner Helmholtz

plane. Adjacent to this inner plane is the outer Helmholtz plane and outside of this is the diffuse layer. A feature of this model is that the electrolyte counter ions are considered to form weak complexes, i.e. *ion pairs* with the oxide surface, i.e.



or



Some stability constants for ion pairs on Fe oxides are listed in Table 10.4. This model was applied by Davis and Leckie (1978, 1980) to adsorption of various cations and anions on ferrihydrite. The extended triple layer model of Sahai and Savenjensky (1997) incorporates recent advances in aqueous electrolyte chemistry which enable aqueous activity coefficients for electrolytes to be calculated over a wide range of ionic strengths. The model also considers the free energy of adsorption of an ion to be the sum of the contributions from an electrostatic term, a Born solvation term and a ion intrinsic term. This extended model has been applied to adsorption of Co and Cd on goethite.

The four layer model (Bowden et al., 1980; Bousse and Meindl, 1986) also locates different adsorbing ions in different planes. It has been used to model adsorption of phosphate, citrate and selenite (Bowden et al., 1980) and borate (Bloesch et al., 1987) on goethite and competitive adsorption of Ca and Cd on ferrihydrite (Cowan et al., 1991).

The CD-MUSIC (Charge distribution multisite complexation model) was developed by the group at Wageningen in the Netherlands (Hiemstra and Van Riemsdijk, 1996). This model is an extension of the MUSIC model (see Chap. 10) which takes into account the abundance of the different types of surface functional groups on the predominant crystal planes of the adsorbent: it is, of course, necessary to be able to identify these planes. A key feature of the model is that the charge is distributed over the entire interfacial region, i.e. over several electrostatic planes. The model appears to have the capacity to accommodate all the experimental information – pH and ionic strength dependency, shifts in iep and changes in zeta potential and proton/ion stoichiometry upon adsorption and also variations in the concentration of the adsorbate – which is needed to provide an adequate picture of the adsorption process. To date, it has been applied to adsorption on goethite of low molecular weight organic acids (Filius et al., 1997), sulphate (Rietra et al., 1999), fulvic acid (Filius et al., 1999), fluoride (Hiemstra and Van Riemsdijk, 2000), chromate (Weerasooriya and Tobschall, 2000), benzene carboxylic acids (Boily et al., 2000) and competitive adsorption of phosphate and citrate (Geelhoed et al., 1998).

The above surface complexation models enable adsorption to be related to such parameters as the number of reactive sites available on the oxide surface, the intrinsic, ionization constants for each type of surface site (see Chap. 10), the capacitance and the binding constants for the adsorbed species. They, therefore, produce adsorption isotherms with a sounder physical basis than do empirical equations such as the Freundlich equation. However, owing to differences in the choice of adjustable

parameters (especially the number of surface sites), they lead to different binding constants and often to different surface complexes (e.g. monodentate vs bidentate and mononuclear vs binuclear) as well (Smith and Jenne, 1991). This means that a comparison of binding constants obtained on different Fe oxides can only be made if the *same* model is used in each case.

The surface complexation models quantify adsorption with experimentally determined equilibrium constants. Another, less widely used approach considers the relationship between the equilibrium constant for the adsorption reaction and the associated free energy change (James and Healy, 1972). Attempts have been made to determine the chemical contribution to the overall adsorption free energy by fitting adsorption isotherms to the experimental data; values of -50 , -33 and -45 kJ mol^{-1} were found for the change in chemical free energy associated with adsorption of Cr, Ni and Zn, respectively, on ferrihydrite (Crawford et al., 1993). Values ranging from -21 to 241 kJ mol^{-1} were found for Ni on hematite; the actual value depended upon the hydrolysis species that were assumed to exist (Fuerstenau and Osseo-Assare, 1987).

Competitive adsorption of ions on Fe oxides is being studied increasingly, owing to its importance in pollutant removal operations (see Chap. 21) and also to its relationship with the availability of nutrients in soils to plants. Progress in predicting the effects of competition is being made, particularly with the more recently developed surface complexation models (Geelhoed et al., 1998; Ali and Dzombak, 1996, 1996a; Lenhart and Honeyman, 1999).

11.3

Anion adsorption

Adsorption of simple inorganic anions, oxyanions and organic ions on iron oxides has been widely investigated (see Tables 11.1 and 11.2). Anions are ligands, i.e. they possess one or more atoms with a lone pair of electrons and so can function as the donor in a coordinate bond. Ligands may adsorb on Fe oxides either specifically or non specifically.

Specific adsorption involves replacement of the surface hydroxyl groups by the adsorbing ligand, L, i.e.



where

$$K_1^s = \frac{\{\equiv \text{FeL}\}}{\{\equiv \text{FeOH}\}[\text{L}^-]} \quad (11.12)$$

$$\beta_2^s = \frac{\{\equiv \text{Fe}_2\text{L}\}}{\{\equiv \text{FeOH}\}^2[\text{L}^-]} \quad (11.13)$$

Tab. 11.1 Inorganic anion adsorption studies on iron oxides.

<i>Oxide</i>	<i>Anion</i>	<i>Reference</i>
Goethite	Arsenate/Arsenite	25, 37, 47, 51, 52, 73, 78, 93
	Borate	14, 29
	Carbonate	77, 86, 87, 92
	Chloride	36
	Chromate	3, 25, 57, 71
	Ferricyanide	81
	Fluoride	35, 36, 38, 48, 74
	Iodate	48
	Molybdate	14, 38, 55, 71
	Phosphate	1, 2, 6, 9, 10, 17, 33, 43, 44, 46, 48, 53, 58, 61, 62, 63, 64, 80, 82, 83
	Selenate/Selenite	11, 18, 28, 33, 34, 37, 50
	Silicate	37, 54, 74
	Sulphate	20, 33, 38, 64, 66, 71, 74, 85, 95
	Tungstate	71
	Vanadate	71
Lepidrocrocite	Phosphate	16, 21, 45, 49
	Sulphate	66
Akaganéite	Sulphate	66
Feroxyhyte	Fluoride	16
	Phosphate	16
Ferrihydrite	Antimonate	73
	Arsenite/Arsenate	26, 40, 42, 68, 69, 89
	Borate	75, 76
	Carbonate	88
	Chromate	39, 58, 91
	Fluoride	16
	Phosphate	27, 30, 60, 72, 88, 90
	Silicate	7, 13, 32, 54, 56, 88
	Sulphate	66
Hematite	Antimonate	4, 5
	Chromate	58
	Molybdate	55, 70
	Fluoride	16
	Phosphate	12, 22, 84
	Selenite	31
	Silicate	13
	Sulphate	19, 41, 64, 66, 79, 85
Magnetite	Chromate	16, 58
	Chloride	8
	Molybdate	55
	Pertechnate	23
Maghemite	Fluoride	16
	Phosphate	16

References for Inorganic Ligands: 1) Ainsworth & Summer, 1985; 2) Ainsworth et al., 1985; 3) Ainsworth et al., 1989; 4) Ambe et al., 1986; 5) Ambe, 1987; 6) Anderson et al., 1985; 7) Anderson & Benjamin, 1985; 8) Ardizzoni et al., 1983; 9) Atkinson et al., 1972; 10) Atkinson et al., 1974; 11) Balistrieri &

Chao, 1987; 12) Barron et al., 1988; 13) Beckwith & Reeve, 1963; 14) Bibak & Borggaard, 1994; 15) Bloesch et al., 1987; 16) Borggaard, 1983 a; 17) Borggaard et al., 1990; 18) Bowden et al., 1980; 19) Breeuwsma & Lyklema, 1973; 20) Brown et al., 1998; 21) Cabrera et al., 1981; 22) Colombo et al., 1994; 23) Cui & Erikson, 1998; 24) Eggleston et al., 1998; 25) Fendorf et al., 1997; 26) Fuller et al., 1993; 27) Gerke, 1993; 28) Glasauer et al., 1995; 29) Goldberg et al., 1993, 1993 a; 30) Gupta, 1976; 31) Hamdy & Gissel-Nielsen, 1977; 32) Hansen et al., 1994; 33) Hansmann & Anderson, 1985; 34) Hayes & Leckie, 1987; 35) Hiemstra & Van Riemsdijk, 2000; 36) Hingston et al., 1968; 37) Hingston et al., 1971; 38) Hingston et al., 1974; 39) Hsia et al., 1993; 40) Hsia et al., 1994; 41) Hug, 1997; 42) Jain et al., 1999; 43) Hie et al., 1995; 44) Jonasson et al., 1988; 45) Lewis & Farmer, 1986; 46) Li & Stanforth, 2000; 47) Lumsdon et al., 1984; 48) Machesky et al., 1991; 49) Madrid et al., 1991; 50) Manceau & Charlet, 1994; 51) Manceau, 1995; 52) Manning et al., 1998; 53) Martin et al., 1988; 54) McKeague & Cline, 1986; 55) McKenzie, 1983; 56) McPhail et al., 1972; 57) Mesuere & Fish, 1992, 1992 a; 58) Music et al., 1986; 59) Nanzyo & Watanabe, 1981, 1982; 60) Nanzyo, 1986; 61) Milsson et al., 1992; 62) Parfitt et al., 1975, 1976; 63) Parfitt & Atkinson, 1976; 64) Parfitt & Russell, 1977; 65) Parfitt & Smart, 1977; 66) Parfitt & Smart, 1978; 67) Persson & Lovgren, 1996; 68) Pierce & Moore, 1980, 1982; 69) Rea et al., 1994; 70) Reyes & Jurinak, 1967; 71) Rietra et al., 1999; 72) Ryden et al., 1977; 73) Schoenfeld & Friedman, 1970; 74) Sigg & Stumm, 1981; 75) Sims & Bigham, 1968; 76) Su & Suarez, 1995; 77) Su & Suarez, 1998; 78) Sun & Donor, 1996; 79) Sugimoto & Wang, 1998; 80) Tejedor-Tejedor & Anderson, 1990; 81) Theis et al., 1988; 82) Torrent et al., 1990; 83) Torrent, 1991; 84) Torrent et al., 1994; 85) Turner & Kramer, 1991, 1992; 86) Van Geen et al., 1994; 87) Villalobos & Leckie, 2001; 88) Watanabe & Matsumoto, 1994; 89) Waychunas et al., 1993; 90) Willet et al., 1988; 91) Zachara et al., 1998; 92) Zeltner & Anderson, 1988; 93) Zhang & Sparks, 1989; 94) Zhang & Sparks, 1990; 95) Zhang & Sparks, 1990a.

Tab. 11.2 Adsorption studies of organic acids on iron oxides.

<i>Oxide</i>	<i>Ligand/molecule</i>	<i>References</i>
Goethite	Benzene-carboxylic acids	5, 12
	Benzoate	20, 37, 38
	Carboxylic acids (in CCl ₄)	3
	Chelidamic acid	1
	Citrate	6, 10, 13
	EDTA	27
	Fulvics	15
	Humics	30, 39
	Hydroxamate	19
	Lactate	10, 13
	Malonate	13, 14
	Oxalate	25, 28, 29
	Phenols	24
	Phthalate	1, 5, 13, 31
	Salicylate	45
	Tartrate	10
	Quinmerac	34
	2,4-D	36, 43
Lepidocrocite	Hydroxybenzenes	7
	2,4-D	23
Akaganéite	Alanine, glycine, serine	18
	EDTA	33
Ferrihydrite	Phenols	24
	Quinmerac	34
	2,4-D	36

Tab. 11.2 (continued)

<i>Oxide</i>	<i>Ligand/molecule</i>	<i>References</i>
Hematite	Benzoate/parabenzoate	20
	Betametasone phosphate	42
	Catchecol	16
	Citrate	46
	Humics	2, 3, 26
	Hydroxypyridine	41
	Iminodiacetic acid	40
	Lauric acid	17
	Oleic acid	17
	Oxalate	18
	Phenols	24
	Phthalate	16
	Polyacrylamide	22
	Potassium octyl hydroxymate	17
	Quinmerac	41
	Thiocyanate	32
Magnetite	Bis (Triethanolammonium)	35
	1–10 Decanedicarboxylate	35
	EDTA	4
	Styrene	44
Maghemite	Hexane	21
	ET ₃ N	21
	Na octylbenzene sulphonate	11
FeO	Styrene	44

References for organic ligands; 1) Ali & Dzombak, 1996; 2) Amal et al. (1992); 3) Avena & Koopal, 1999; 4) Blesa et al., 1984; 5) Boily et al., 2000; 6) Bowden et al., 1980; 7) Bromley et al., 1994; 8) Buckland et al., 1980; 9) Chang et al., 1983; 10) Cornell & Schindler, 1980; 11) Dao et al., 1998; 12) Evanko & Dzombak, 1998, 1999; 13) Filius et al., 1997; 14) Filius et al., 1999; 15) Filius et al., 2000; 16) Gu et al., 1995; 17) Han et al., 1973; 18) Holm et al., 1983; 19) Holmen et al., 1997; 20) Kung & McBride, 1989, 1989a; 21) Kuznetsov et al., 1993; 22) Lee & Somasundaran, 1989; 23) Madrid & Diaz-Barrientos, 1991; 24) McBride & Kung, 1991; 25) Mesure & Fish, 1992; 26) Murphy et al., 1992; 27) Nowack & Sigg, 1996; 28) Parfitt & Russell, 1977; 29) Parfitt et al., 1977; 30) Parfitt et al., 1977a; 31) Persson et al., 1998; 32) Regazzoni et al., 1991; 33) Rubio & Matijevic, 1979; 34) Schwandt et al., 1992; 35) Sköld & Tunius, 1994; 36) Sticher & Augustoni-Phan, 1977; 37) Tejedor-Tejedor et al., 1990; 38) Tejedor-Tejedor et al., 1992; 39) Tipping & Cooke, 1982; 40) Torres et al., 1988; 41) Vasudevan et al., 2001; 42) Vera et al., 1997; 43) Watson et al., 1973; 44) Wühn et al., 2000; 45) Zeltner et al., 1986; 46) Zhang et al., 1985.

It is also termed chemisorption (especially for gases), inner sphere adsorption and, in the case of ligands, ligand exchange. The binding constants, K_1^s and β_2^s for the surface complexes show the same stability trend as do the constants for the equivalent complexation reactions in solution.

As seen from the above equations, specific adsorption involves direct coordination of the adsorbing species to the surface metal atom of the solid, i.e. there is no solvent molecule between the adsorbed species and the surface. Thus, the linkage has a large proportion of covalent character. The chemical component of the adsorption free energy predominates; as a result, adsorption may take place on a neutral surface

or even one with the same charge as the adsorbing species. Specifically adsorbing ions modify the surface charge on the oxide and hence, cause a shift in the pzc/iep (see Chap. 10). They are usually tightly bound and not easily displaced. Anions that adsorb specifically on iron oxides include phosphate, silicate, selenite, arsenite, chloride, fluoride, citrate and oxalate.

Non specific adsorption is also termed ion pair formation and outer sphere adsorption. It is dominated by the electrostatic contribution to the free energy of adsorption and hence, is influenced by the ionic strength of the system. The adsorbing species retains its primary hydration shell, i.e. at least one water molecule is interposed between the anion and the surface. For weak organic acids, outer sphere complexation can involve a hydrogen bond between the carboxylate or hydroxyl group of the adsorbate and the singly or triply coordinated surface groups on goethite (Filius et al., 1997). In a multicomponent system, nonspecifically adsorbing ions of the same charge are taken up in proportion to their concentrations in solution. They are readily replaced by other anions and this type of adsorption on iron oxides has, therefore, been treated in some cases as a form of ion exchange (Paterson and Rahman, 1984, 1984a). Examples of nonspecifically adsorbing anions include nitrate and perchlorate ions. Salts of these ions are, therefore, suitable for use as inert electrolytes in surface chemistry studies.

Adsorption of anions on oxides is usually accompanied by the uptake of protons (or the release of hydroxyl ions). The ratio between the number of protons that are coadsorbed and the level of anion adsorption is not usually stoichiometric. Studies of adsorption of oxyanions on goethite as a function of pH appear to indicate that, provided only *one* adsorbed species is present, the proton: anion ratio is related to the mode of adsorption (Rietra et al., 1999). It follows that oxyanions which adsorb with a similar proton/anion stoichiometry, have a similar adsorption mechanism.

Anion adsorption at any pH increases with rising concentration of the adsorbing species. The adsorption isotherms frequently display Langmuirian behaviour and this is considered to indicate that only one type of adsorption site is involved; for iron oxides this is the singly coordinated surface hydroxyl group. Adsorption is at a maximum at low pH and decreases with rising pH except for silicate (Fig. 11.1). For non-specifically adsorbing anions, adsorption is negligible above the pzc. The relationship between pH and the apparent Langmuir maximum for anion adsorption is termed the adsorption envelope. Some authors reported that the adsorption envelope on goethite displayed maxima or discontinuities at the pKa(s) of the conjugate acid of the adsorbing anion. For fluoride and silicate, maxima occurred at pH 4 and pH 7, respectively; for phosphate there were discontinuities at pH 7 and pH 12 (Hingston et al., 1967, 1968). These breaks or maxima are not always well defined; Sigg and Stumm (1981) reported a gradual decrease with rising pH of the adsorption envelope of phosphate on goethite.

The effect of rising pH on anion adsorption is the result of two opposing effects: 1) the increase in the relative concentration of the anionic form(s) of the conjugate acid as the pK_a is approached which promotes adsorption on the oppositely charged surface, 2) the decrease with rising pH in the number of surface FeOH₂⁺ groups. The maximum in the adsorption envelope for fluoride and the breaks or slope changes

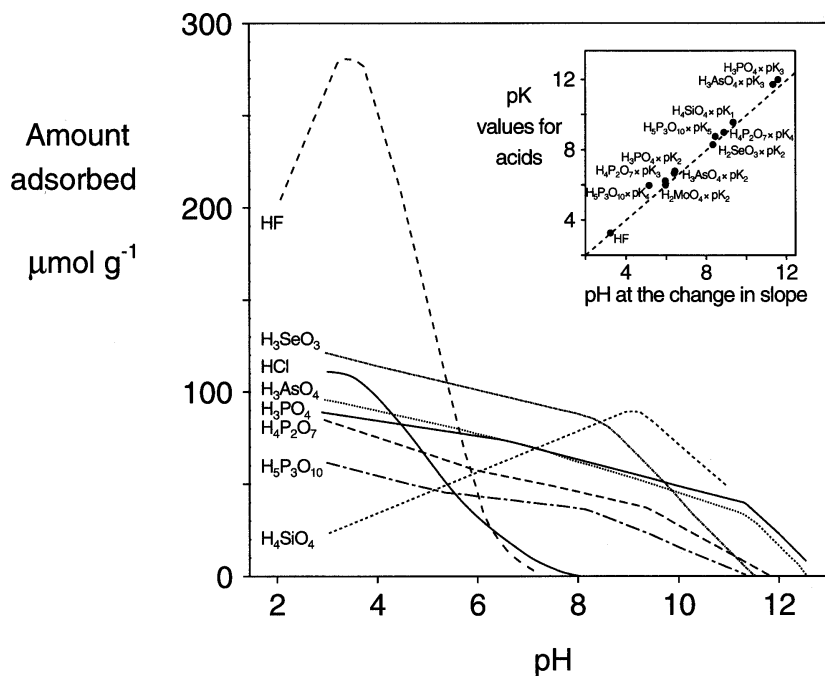
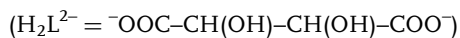


Fig. 11.1 Effect of pH on the adsorption of various anions on goethite together with a plot of the amount adsorbed vs. pK_a values of the respective acids (Hingston et al., 1968, with permission).

for the polyprotic acids correspond to the highest concentration of the complex at the surface; this is the product of the number of surface sites and the concentration of suitable anionic species, i.e. $\equiv[\text{FeL}] = [\equiv\text{FeOH}][\text{HL}]$. When electrostatics govern adsorption (i.e. nonspecific adsorption), the surface must have an overall positive charge in order for adsorption to take place, hence, the region of maximum adsorption lies between the pK_a of the acid and the pzc of the solid. In contrast, where specific adsorption is involved, an overall positive surface charge is not required (only FeOH_2^+ and FeOH groups), which explains why adsorption can occur at pH's above the pzc. Polyprotic acids such as silicate and phosphate that can form more than one species in solution adsorb over a wider pH range. Molecules with functional groups with high pK_a s (e.g. OH groups) adsorb at high pH and increase the negative charge of the surface.

The acidity of organic ligands is enhanced by coordination with the oxide surface, i.e. the surface promotes deprotonation of the functional groups (COOH or OH). Such ligands, therefore, adsorb on the surface at a pH 2–3 units lower than that at which complexation with Fe in solution would occur (Kummert and Stumm, 1980). An example of this is the deprotonation of the alcoholic OH group of tartaric acid upon adsorption on the goethite surface (Cornell and Schindler, 1980). The appropriate reaction for the acid in water is,



This equation can be combined with that for protonation of the surface OH groups on goethite (Lovgren et al., 1990),



to give the tartaric acid/goethite interaction reaction,



which shows that the deprotonation of the alcoholic hydroxyl groups of tartaric acid is promoted by the surface OH groups on the oxide.

Adsorption of anions is usually a two-step process with a rapid, initial stage (minutes to hours) limited mainly by diffusion of adsorbing species to readily accessible sites. The second, slower stage, which may take days, has been attributed to various factors including diffusion into particle aggregates (Willet et al., 1988; Fuller et al., 1993) or crystal micropores and to structural rearrangement of the surface complexes. The kinetics of the initial stage have been followed by isotope exchange measurements (Atkinson et al., 1972) and by pressure jump techniques (Astumian et al., 1981; Hayes and Leckie, 1986; Grossl et al., 1997).

Calorimetric techniques have been used to measure heats of anion adsorption; to date, the available data is limited and somewhat contradictory. The free enthalpy of adsorption often decreases as surface coverage rises, and at least initially, is exothermic (Zeltner et al., 1986; Machesky et al., 1989). Adsorption enthalpies may provide information about site heterogeneity and the temperature dependence of adsorption. The available data suggest that adsorption increases with rising temperature. Uptake of oxalate on hematite rose slightly as the temperature increased from 20 to 60 °C (Zhang et al., 1985) and adsorption of the antimonate ion increased over the range 30–60 °C with an activation energy of 37 kJ mol⁻¹ (Ambe et al., 1986; Ambe, 1987). Using a modified Freundlich equation, Torrent (1991) obtained activation energies of between 38 and 80 kJ mol⁻¹ for the slow reaction of phosphate with goethite (15 samples).

The desorption of anions from iron oxides as a result of changing the anion concentration in solution is often very slow. It can be accelerated by increasing the pH. The partial irreversibility of anion adsorption has been attributed by some authors to a high activation energy of adsorption resulting from the formation of multidentate surface complexes, whereas others attribute it to a slow diffusion out of micropores.

11.3.1

Modes of Coordination

Simple ligands can adsorb on iron oxides to form a variety of surface species including mononuclear monodentate, mononuclear bidentate and binuclear mono or bidentate complexes (Fig. 11.2): these complexes may also be protonated. How adsorbed ligands (and cations) are coordinated to the oxide surface can be deduced from adsorption data, particularly from the area/adsorbed species and from coadsorption of protons. Spectroscopic techniques such as FTIR and EXAFS can provide further (often direct) information about the nature of the surface species and their mode of coordination. In another approach, the surface species which permit satisfactory modelling of the adsorption data are often assumed to predominate. As, however, the species chosen can depend upon the model being used, this method cannot provide an unequivocal indication of surface speciation; confirmation by an experimental (preferably spectroscopic) technique is necessary.

The halide ions adsorb on Fe oxides as monodentate complexes (Parfitt & Russell, 1977). IR spectroscopy showed that acetic acid and dodecanoic acid form mononuclear surface complexes on goethite whether they adsorb from the vapour phase or from CCl_4 solution (Buckland et al., 1980). At low levels of adsorption, oxalate forms binuclear surface complexes on goethite, but as the surface coverage approaches saturation, the mode of coordination changes to permit increased adsorption (Parfitt et al., 1977). Similar behaviour was reported for succinic and dodecyl succinic acid: at high surface coverage, steric hindrance involving the long chain of the molecule prevented bidentate coordination (Buckland et al., 1980). Cylindrical internal reflectance (CIR) FTIR showed that the benzoate ion forms a binuclear complex on goethite (Tejedor-Tejedor et al., 1990) and phthalate forms both mono and bidentate complexes (Tejedor-Tejedor et al., 1992). Salicylate adsorption involves one COOH and one OH group (Yost et al., 1990; Biber and Stumm, 1994), whereas chelidamic acid adsorbs through COOH and nitrogen groups (Davis and Leckie, 1978; Ali and Dzombak, 1996).

EXAFS data showed that cations and oxyanions (e.g. selenite and arsenite) can form two kinds of bidentate, inner sphere complexes on iron oxides depending upon the surface site at which the adsorbate adsorbs (Manceau, 1995; Randall et al.,

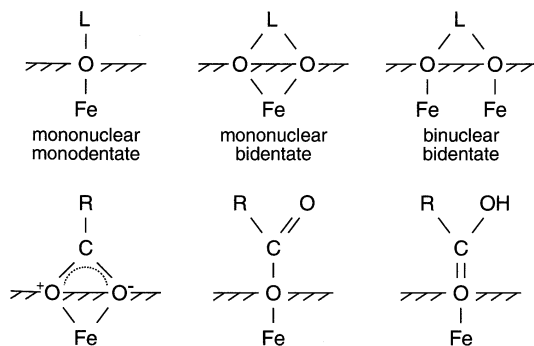


Fig. 11.2 Modes of ligand coordination to the iron oxide surface and modes of coordination through COOH groups.

1999). A binuclear, bidentate complex binds to the surface hydroxyls at the *corners* of two adjacent $\text{Fe}(\text{OH})_6$ octahedra. Such a site is termed a double corner linkage (^2C) and predominates on the (101) planes on goethite. The mononuclear, bidentate complex, on the other hand, binds to the groups along the *edge* of an $\text{Fe}(\text{OH})_6$ octahedron and so is termed an edge linkage (^2E). These edge sites are considered to be high energy sites which are preferentially occupied at low surface coverages. Both types of site are illustrated in Fig. 11.3. The ratio of edge sites to corner sites is much greater for ferrihydrite and lepidocrocite than it is for goethite and is considered to be responsible for differences in the types of surface complexes found on different Fe oxides (Manceau et al., 2000).

For some of the most intensively studied anions, increased information has not clarified the speciation or coordination of the adsorbed complex. For example, on the basis of IR data it has been claimed that sulphate adsorbs on goethite as both a bidentate and a monodentate surface complex (Parfitt and Smart, 1977; Persson and Lovgren, 1996). Some of the conflict may arise from differences in the conditions under which the experiments were carried out. Most IR spectroscopy measurements of adsorbed sulphate on Fe oxides were made on dried samples. Hug (1997) compared

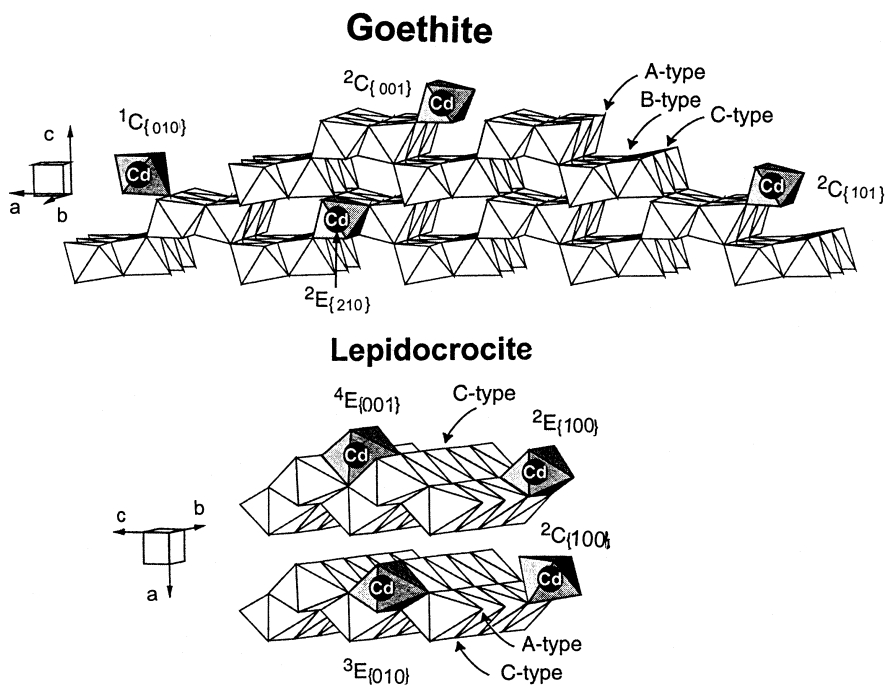


Fig. 11.3 Surface complex of octahedrally coordinated Cd on a) goethite and b) lepidocrocite. The Cd surface complex can be bonded to either the edge (E) or vertex (C) of one octahedron. For each type of complex (e.g. $^2\text{C}_{(001)}$), the super-

script indicates the number of bonds between the Fe and Cd octahedra and the subscript indicates the crystallographic plane to which the complex is bound (Manceau et al., 2000; with permission).

the spectra of sulphate adsorbed on hematite particles (14 nm diameter) under both wet and dry conditions and found that at low pH in aqueous media, sulphate adsorbs as an inner sphere, monodentate complex. Upon drying the sample, another band appeared in the IR spectrum suggesting (to earlier workers) a bidentate species. Similar results were found subsequently for goethite (Peak et al., 1999). With a combination of Raman and ATR/FTIR spectroscopy, Wijna and Schulthess (2000) showed that on goethite, sulphate forms a monodentate surface complex which is inner sphere at pH 3–6, but outer sphere at higher pH. With the CD-MUSIC model, sulphate adsorption on goethite at pH 3–8 over a range of surface coverages and ionic strengths could be described by one (inner-sphere), monodentate complex (Rietra et al., 1999). However, Sugimoto and Wang (1998) reported that in both wet and dry systems, sulphate adsorbed on hematite as a bidentate complex at pH < 1. These authors also found that adsorption/unit area depended upon hematite morphology and decreased in the order; ellipsoids > pseudocubes > thick plates > thin plates. This behaviour was attributed to preferential adsorption on the {012} planes, the extent of development of which was different for different morphologies. Blesa et al. (2000) suggested that a sequence of transformations or rearrangements may be involved before the final structure of a complex is adopted. Similarly, Eggleston et al. (1998) suggested, on the basis of STM examination of sulphate adsorption on hematite, that each species that is detected might be the *average* of a range of highly mobile, slightly different complexes. Su et al. (1997) also point out that pure inner and outer sphere complexes may be the end members in some systems, but that in others a *mixture* of species, some protonated and some not, may result in a system with an average protonation value. These possibilities must be borne in mind when comparing conflicting data. Ideally, a range of experimental conditions and at least two experimental techniques, combined with modelling, should be applied to the investigation of adsorption of species on Fe oxides – and this approach is being increasingly adopted.

11.3.2

Examples of Inorganic Ligands

11.3.2.1 Phosphate

The most widely investigated of inorganic ligands that adsorb on Fe oxides is phosphate. This ligand adsorbs specifically and this behaviour strongly affects the availability of phosphate to plants (Guzman et al., 1994). Owing to the polyprotic character of this ligand, adsorption takes place over a wide pH range. It is at a maximum at low pH and decreases gradually as the pH rises with the slope of the adsorption envelope changing at each pK_a value of the acid (Fig. 11.1) (Hingston et al., 1972; Breeuswma, 1973; Sigg & Stumm, 1981).

Adsorption of phosphate is initially rapid and is followed by a slow stage (hours to days) that is more pronounced for less crystalline samples of Fe oxides (Barrow et al., 1981; Torrent et al., 1990; Nilsson et al., 1992). The slow stage has been attributed to diffusion into micropores or grooves (Torrent, 1991; Strauss et al., 1997) and into aggregates of particles (Anderson et al., 1985; Willet et al., 1988). Evidence for slow dif-

fusion into meso and micropores between domains in crystals comes from a kinetic study involving goethites with different crystallinities (Strauss et al., 1997). Adsorption, at room temperature, on goethite the crystallinity of which had been improved by hydrothermal treatment, was complete within 24 hr, whereas the extent and rate of adsorption on untreated goethites was much lower and dependent on the crystallinity of the samples; in one case adsorption was complete only after three weeks. This long term adsorption was modelled using the equations for diffusion into a cylinder. Previously, the kinetics of heterogeneous isotope exchange between phosphate in solution and that on the surface of goethite was described by the Elovich equation (Atkinson et al., 1972); the rate constant for P exchange ($1-27 \cdot 10^{-3} \text{ min}^{-1}$) is much lower than that for exchange with metal/P complexes in solution. Desorption of phosphate from goethite is very slow and partly irreversible. Torrent et al. (1990; 1992), for example, found that only 84% of adsorbed phosphate could be desorbed from goethite in 0.1 M KOH after 16 hr at room temperature: even less desorbed from microporous goethite. This behaviour was attributed both to slow rediffusion out of the micropores and also to formation of inert, binuclear surface complexes (Atkinson et al., 1972). A combination of TEM, BET and isotope exchange measurement indicated that adsorbed phosphate can link goethite crystals into aggregates (Anderson et al., 1985): this could be a further cause of partly irreversible adsorption.

Adsorption of phosphate on Fe oxides involves a ligand exchange mechanism (Parfitt and Russell, 1977; Sigg and Stumm, 1981) and appears to be promoted by increasing the ionic strength (Bowden et al., 1980). Spectroscopic studies have not provided an entirely consistent picture of the mode of phosphate adsorption, but the consensus from studies with a range of techniques is, that phosphate adsorbs on Fe oxides predominantly as a binuclear, bidentate complex.

Rietra et al. (1999a) found very similar macroscopic, proton/ion ratios for adsorption of both phosphate and arsenate on goethite and as EXAFS data showed that arsenate adsorbed as a bidentate complex, they concluded that phosphate behaved similarly. IR studies showed that on goethite, each phosphate ion replaces two, singly coordinated surface OH groups to form a bridging, binuclear surface complex (Parfitt et al., 1975; Nanzoy, 1986; Torrent et al., 1990). This is shown schematically in Figure 11.4 for the (most frequently occurring) (101) crystal face of goethite. Similar complexes form on lepidocrocite, akaganéite and ferrihydrite (Atkinson et al., 1974; Parfitt et al., 1976; Nanzoy and Watanabe, 1982; Barron et al., 1988). ATR-FTIR measurements suggest a non protonated, bidentate binuclear surface complex on ferrihydrite at pH > 7.5 and a protonated complex at pH 4–6 (Arai and Sparks, 2001). Various authors nevertheless, present data supporting monodentate surface complexes. From DRIFT FTIR data, Persson et al. (1990) proposed that there were three types of monodentate surface complexes with different degrees of protonation. There are suggestions that the mode of coordination changes from bidentate to monodentate at high surface coverages or as the pH varies (Sigg and Stumm, 1980; Goldberg and Sposito, 1984; Nilsson, 1992 (all titration studies); Tejedor-Tejedor and Anderson, 1990 (CIR/FTIR); Jie et al., 1995). Hiemstra and Van Riemsdijk (1996) modelled phosphate adsorption on goethite with the CD-MUSIC model using comparable experimental data taken from several sources so as to provide a large enough

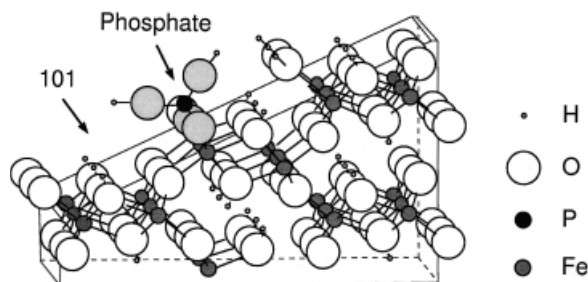


Fig. 11.4 Surface complex of tetrahedrally coordinated phosphate (hatched) through two neighbouring, singly coordinated Fe-OH groups on the (101) face of goethite (Stanjek, unpubl.).

data set. They concluded that the monodentate species could exist, but only at very low surface loadings. Geelhoed et al. (1998) used a combination of surface complexes to model the adsorption data of Tejedor-Tejedor et al. (1990) for phosphate adsorption on goethite and concluded that at low to intermediate pH, the bidentate surface complex was the most abundant.

In acidic and neutral media, the maximum sorption capacity of synthetic goethite for phosphate is ca. $2.5 \mu\text{mol m}^{-2}$ (Hingston, 1981; Cabrera et al., 1981; Borggaard 1993 a; Ainsworth et al., 1985; Torrent et al., 1990; Strauss et al., 1997). This corresponds to an adsorption density of one phosphate per 0.66 nm^2 which is very close to the area occupied by two singly coordinated OH groups on the (101) plane (0.68 nm^2 , see Table 10.1) which strongly supports a bidentate complex at close to saturation coverage. The phosphate sorption capacity is essentially the same per unit area for synthetic and natural goethites with a range of morphologies. This is attributed to the fact that the predominant face on all goethites is (101) (see Chap. 4). For 31 synthetic goethites ($21\text{--}115 \text{ m}^2 \text{ g}^{-1}$) the relationship between P adsorption and surface area was (Torrent et al., 1990):

$$P_{\text{ads}} (\mu\text{mol g}^{-1}) = 2.50 \text{ SA } (\text{m}^2 \text{ g}^{-1}) - 0.37 \quad (n = 31; r^2 = 0.939)$$

In contrast, there is no clear correlation between surface area and the extent of phosphate adsorption on hematites because adsorption is face-specific; hematites grown under different conditions display different sets of planes (see Chap. 4) and these in turn exhibit different sets of functional groups (see Chap. 10). Pairs of singly coordinated hydroxyls are located on the (110), (100), (012) and (113) faces, but not on other common planes such as (104) and (001); the latter are most probably inactive with respect to adsorption. The adsorption capacity, therefore, depends on crystal morphology; rhombohedral crystals are reported to adsorb more per unit of surface area than platy ones. For a set of 43 synthetic hematites with widely different morphologies, the mean Langmuir adsorption maximum was $0.98 \pm 0.69 \mu\text{mol m}^{-2}$ (Barrón et al., 1988). Another set of 30 hematites, with varying Al-for-Fe substitution, showed an average capacity of $1.03 \pm 0.53 \mu\text{mol m}^{-2}$ after 124 days (Colombo et al.,

1994). It is obvious that the standard deviation for hematites is greater than that for goethites, mainly due to the greater variety of crystal faces. Al-for-Fe substitution did not directly influence the P adsorption for either synthetic goethites or hematites; the surface area tends to increase with rising Al incorporation and this, in turn, increases adsorption/unit weight (Ainsworth et al., 1985).

Interaction of phosphate solutions with goethite may lead to surface precipitation of phosphates if the concentration of P in solution exceeds the mineral solubility (Jonasson et al., 1988). A combined Auger, XPS, scanning SIMS and electron diffraction study showed that after 90 days at 60 °C, crystals of griphite (an Fe hydroxy phosphate) precipitated out of a phosphate solution onto crystals of goethite (Martin et al., 1988).

11.3.2.2 Other Anions

Only a few studies dealing with *silicate* adsorption on Fe oxides exist, possibly because polymerization of this anion complicates interpretation of its behaviour. The adsorption maximum on goethite (ca. 3 $\mu\text{mol m}^{-2}$) found by Hingston et al. (1967) at the pH of the pK_1 of silicic acid (~ 9) was also reported by Sigg and Stumm (1981). They obtained an intrinsic adsorption constant ($\log K$) for H_3SiO_4^- of 4.1, and for $\text{H}_2\text{SiO}_4^{2-}$ of -3.3 . For ferrihydrite, equilibration with silicate was, in contrast to proton adsorption, rather slow (weeks). The adsorption constant was calculated, using a two-layer model, to be $\log K_{\text{Si}} = 3.62$ for the species $\equiv \text{FeOSi}(\text{OH})_3$ (Hansen et al., 1994). Twice as much Si was adsorbed at pH 5 as at pH 3. The Si-O-stretching IR vibration at 940–960 cm^{-1} in Si-ferrihydrite is considered to be due to Fe-O-Si bonding, and its shift to higher wavenumbers as adsorbed Si rose may indicate an increasing interaction between silicate species i.e. polymerization. This was also observed by other workers with synthetic and natural ferrihydrites (Schwertmann and Fischer, 1973; Carlson and Schwertmann, 1981; Anderson and Benjamin, 1985; Childs et al., 1986; Cornell et al., 1987; Vempati and Loeppert, 1989; Parfitt et al., 1992). A transition from adsorption to surface precipitation leads to surface coating as shown for silicate on hematite (Ohmori and Matijevic, 1992).

Adsorption of *chromate* (Cr^{VI}), has been widely investigated because chromate is a toxic waste product of many industrial processes. Adsorption of the chromate ion (CrO_4^{2-}) is at a maximum between pH 3 to 6 on all Fe oxides studied and falls off rapidly at higher pH (Music et al., 1986). Adsorption is very high (0.1 $\mu\text{mol Cr mol}^{-1}$ Fe) on ferrihydrite at pH 5.5 (Leckie et al., 1980). Chromate has been considered to be intermediate in binding capacity on Fe oxides between strongly (e.g. phosphate) and weakly adsorbing anions (Mesure and Fish, 1992). Earlier workers considered adsorption to involve an outer sphere complex (Davis and Leckie, 1980; Hayes et al., 1988; Ainsworth et al., 1989; Zachara et al., 1989), but later studies involving FTIR, EXAFS, electrophoresis and measurement of shifts of iep, support an inner sphere mechanism (Hsia et al., 1993; Fendorf et al., 1997). Support for inner sphere complexation also came from modelling of data with the CD-MUSIC model (Weerasooriya and Tobschall, 2000). Grossl et al. (1997) suggested, on the basis of pressure jump, relaxation kinetics data, that adsorption on goethite involved rapid ligand exchange to form a monodentate complex, followed by a slower step in which the in-

itial surface species rearranged to form a bidentate complex. Silicate, sulphate and dissolved CO_2 (all at 10^{-3} M) reduced chromate (10^{-6} M) adsorption on ferrihydrite, whereas similar levels of K^+ , Ca^{2+} and Mg^{2+} had no effect (Zachara et al., 1987).

Trace amounts of chromate ions adsorbed on magnetite are reduced to Cr^{III} by the surface Fe^{II} ions (Music et al., 1986; Peterson et al., 1996, 1997a; Kendlewicz et al., 1999). A solid state reaction in which the surface layers of magnetite are converted into maghemite appears to be involved: as more chromate is adsorbed, further reduction is halted (Peterson et al., 1996). XAS showed that although adsorbed chromate was not reduced on the (112) plane of hematite, small amounts were reduced on (001): it was suggested that some Fe^{II} had been produced on the latter plane during annealing under vacuum (Kendlewicz et al., 1999).

Chromate adsorbed from solution by green rust was reduced to Cr^{III} with the green rust being simultaneously converted to ferrihydrite or possibly a Cr substituted ferrihydrite (Loyaux-Launiezak et al., 2000).

The *selenite* and *selenate* ions illustrate the effect of oxidation state on adsorption behaviour. The selenite ion (SeO_3^{2-}) adsorbs strongly and specifically on goethite and shifts the iep of both goethite and ferrihydrite to lower pH values (Su and Suarez, 2000). Adsorption is at a maximum in the acid region and decreases to negligible values above pH 10 (Hingston et al., 1968a, 1971; Balistrieri and Chao, 1987). It is largely irreversible. Glasauer et al. (1995) measured adsorption of selenite on six goethites at pH ca. 5 in a flow through reaction chamber and found that neither the electrolyte anion (Cl^- or SO_4^{2-}) nor the morphology of the goethite (mono- versus multidomainic) affected the extent or rate of adsorption. Selenate has a much lower affinity for Fe oxides than does selenite; it does not adsorb above pH 7. Hingston (1974) reported that it is easily desorbed from goethite by washing, although Suarez et al. (1999) claimed that it could not be desorbed from ferrihydrite. The intrinsic rate constants for adsorption on and desorption from goethite are $3.52 \cdot 10^8 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ and 3.34 s^{-1} , respectively (Zhang and Sparks, 1990). EXAFS data showed that selenite adsorbs on Fe oxides as an inner sphere, binuclear complex (Hayes et al., 1987; Manceau and Charlet, 1994), but there is some controversy about the meaning of this data for selenate; it appears to support both an outer sphere complex (Hayes et al., 1987) and an inner sphere complex (Manceau and Charlet, 1994). IR data also supported an inner sphere complex (Harrison and Berkheiser, 1982). A recent application of Raman spectroscopy to selenate adsorption on goethite appears to indicate that pH may be the deciding factor with an inner sphere complex forming at low pH and an outer sphere one above pH 6 (Wijna and Schulthess, 2000).

Both *arsenate* (As^{V}) and *arsenite* (As^{III}) are toxic (As^{III} more so than As^{V}), and both are adsorbed by Fe oxides. Fifty mg of 2-line ferrihydrite, for example, adsorbed 98%, 75% and 20% arsenate from 50 ml of 0.1, 1.0 and 5.0 mM As^{V} solution, respectively, at pH 6.8 and 23 °C (Langer and Inskeep, 2000). Adsorption of both forms of arsenic on Fe oxides appears to be Langmuirian (Fergusson and Gavis, 1972; Holm et al., 1979). Adsorption is strongly pH dependent, but whereas adsorption of arsenate is greater at low pH, that of arsenite increases with rising pH (Pierce and Moore, 1980, 1982; Manning et al., 1998). At pH 4.6, the maximum adsorption on 2-line ferrihydrite was ca. 0.6 and 0.25 mol As/mol Fe for arsenite and arsenate, re-

spectively and similarly, at pH 9.2, the maximum adsorbed was 0.58 and 0.16 mol As/mol Fe (Raven et al., 1998). The adsorption envelopes cross in the region 6–7.5 and this is attributed to differences in the types of surface complexes formed by the two oxidation states. Both arsenite and arsenate form inner sphere complexes on Fe oxides and many studies support the existence of binculear species (Hingston et al., 1971; Anderson and Malotsky, 1979; Lumsdon et al., 1984; Waychunas et al., 1993, 1994; Manceau 1995; Sun and Donor, 1996, 1998; O'Reilly et al., 2001). Suarez et al., 1998, concluded, on the basis of electrophoretic mobility data and OH^- release measurements, that on ferrihydrite, a bidentate AsO_4^{3-} surface complex was consistent with earlier EXAFS, iep shift and sorption data, but conflicted with IR data which required a monodentate, protonated complex. Jain et al. (1999) measured the H^+/OH^- stoichiometry during adsorption of both As^{V} and As^{III} on ferrihydrite (pH 4–10) and reported that the amount of H^+ or OH^- released per mol As^{III} adsorbed, varied with surface coverage with a monodentate complex being present above pH 8. The EXAFS results of Fendorf et al. (1997) also suggested that as the extent of adsorption on goethite rose, the speciation of arsenate changed from monodentate to bidentate. A combination of Raman, FTIR and electrophoretic mobility measurements supports the formation of both inner and outer sphere complexes of arsenite on ferrihydrite, depending upon the pH (Goldberg and Johnston, 2001). Arsenate adsorbs on a sulphate green rust as an inner sphere complex (Randall et al., 2001).

The kinetics of arsenate adsorption on goethite appears to involve a two stage mechanism (Grossl et al., 1997). Arsenite adsorption on hematite is fast with equilibrium being reached in less than one hour; the kinetics were first order (Singh et al., 1988). Initial rapid adsorption of arsenate on ferrihydrite was followed by much slower adsorption, the rate of which was limited by intra-particle diffusion; the kinetics data fitted the Elovich equation (Fuller et al., 1993). O'Reilly et al. (2001) report, however, that sorption of arsenate on ferrihydrite after 12 months is only 10% greater than that after 4 min which suggests that the slow stage makes only a small contribution to the overall process.

Adsorption of *borate* on goethite is reversible with respect to both pH and concentration; desorption is promoted by raising the temperature, whereas temperature (10–40 °C) has only a weak effect on adsorption (Bloesch et al., 1987). Adsorption on goethite was at a maximum at pH 8–9 (Goldberg et al., 1993a), whereas on ferrihydrite, it peaked at pH 6.5–8.5 (Su and Suarez, 1995). Borate lowered the iep of ferrihydrite from 8.6 to 6.8. FTIR spectra suggested that adsorption involved ligand exchange and two adsorbing species – $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ (Su and Suarez, 1995). The high level of *tellurate* associated with ferrihydrite (ca. 4 mM g^{-1}) indicates that this octahedral anion probably forms a surface coating rather than adsorbed complexes (Harrison and Berkheiser, 1982).

Adsorption of *fluoride* on goethite falls as the pH rises. Where adsorption is low, it involves ligand exchange with singly coordinated surface hydroxyl groups, whereas at higher levels, other surface hydroxyl groups may be involved (Hiemstra and Van Riemsdijk, 2000). At very high fluoride concentrations and low pH, surface precipitation of FeF_3 takes place: this is promoted by high ionic strength.

Adsorption of ferricyanide (a contaminant of sites of former gas plants) on goethite decreases with rising pH and is dependent on ionic strength: it is fully reversible and is thought to involve both inner and outer sphere complexes. Adsorption of ferrocyanide on goethite involves initial formation of inner sphere complexes followed by precipitation of a Berlin Blue-like phase on the goethite surface (Rennert and Mansfeldt, 2001).

11.3.2.3 Organic Anions and other Organic Compounds

Investigations of the adsorption of organic compounds on iron oxides have been prompted by the role of chelating agents such as citrate and oxalate in rust removal, by the application of fatty acids, e.g. oleic acid, as surfactants and flotation agents, by the adsorption of pesticides in soils and by the effect of organic molecules on the properties of iron oxides in soils. These studies have considered the effects of organic acids, amines, sugars, phosphonates, fatty acids, phenols and a range of aromatic compounds (Table 11.2).

Adsorption of organic ligands on Fe oxides is usually dominated by electrostatic effects, although ligand exchange and hydrogen bonding may also be involved (Schindler, 1990). Uptake is therefore, commonly at a maximum at pHs where the oxide surface is positively charged, i.e. at pHs < pzc/iep.

Adsorption of *oxalate* on Fe oxides is rapid (Parfitt et al., 1977). This ligand shifted the iep of hematite from 7.6 to 2.7 and increased the electrophoretic mobility of the oxide at pHs above the iep (Kallay and Matijevic, 1985). The maximum sorption capacity of hematite for oxalate was $20 \mu\text{mol m}^{-2}$, whereas for goethite it was much lower, viz. $4 \mu\text{mol m}^{-2}$ (Parfitt et al., 1977; Zhang et al., 1985). Adsorption of oxalate on goethite at pH 3–7.5 could be modelled using the CD-MUSIC model with only one adsorbing species (Filius et al., 1997). Adsorption of lactate, tartrate and citrate on goethite is highest at ca. pH 3 and falls with rising pH; the lactate ion does not adsorb at pH 8, whereas tartrate and citrate adsorb up to pH 9–10 (Cornell and Schindler, 1980). The maximum level of citrate adsorbed on goethite ($1.9 \mu\text{mol m}^{-2}$) was lower than that adsorbed on hematite ($3.6 \mu\text{mol m}^{-2}$) (Cornell and Schindler, 1980; Kallay and Matijevic, 1985).

Filius et al. (1997) modelled the adsorption data for a range of *organic acids* on goethite with the CD-MUSIC model and concluded that lactate uptake, which was weak, was due entirely to electrostatic forces and involved an outer sphere complex with additional hydrogen bonding with the surface hydroxyl groups. Citrate formed an inner sphere complex, but whereas earlier adsorption and IR data supported a tridentate complex (Cornell and Schindler, 1980), modelling work gave a better fit with a bidentate complex (Filius et al., 1997): the extent of deprotonation of the complex depended on the pH of the system and rose with increasing pH. Where the experimental data covered a range of experimental conditions, more than one type of surface complex for lactate and citrate was needed to model the data over the whole range of pHs, ionic strengths and adsorbate concentrations. Modelling also suggested that where adsorption was influenced by ionic strength (e.g. for lactate), ion pair formation involving the uncoordinated carboxyl group of the adsorbate ion and the cation of the electrolyte, was important.

Adsorption of *EDTA* on hematite and akaganéite is Langmuirian with maximum adsorption occurring at pH 3 and falling to nearly zero at pH 8.5 (akaganéite) or pH 9.6 (hematite) (Rubio and Matijevic, 1979; Chang et al., 1983). Related chelating agents – DTPA, CDTA and NTA – adsorbed similarly on hematite (Chang et al., 1983). The free energy of adsorption of these organics ranged from -38 to -32 kJ mol $^{-1}$ (pH 3–7) for akaganéite and from -27.3 – 17.06 kJ mol $^{-1}$ (pH 2.7–8.0) for hematite.

A large range of *aromatic acids* with up to six carboxyl or carboxyl and/or phenolic groups in different positions on the benzene ring was adsorbed on goethite (pH 3–9) in an attempt to mimic the behaviour of natural organic matter (NOM) (Evanko and Dzombak, 1998, 1999). Adsorption increased as the number of COOH groups on the benzene ring increased being very low for benzoic acid, moderate for phthalic acid (two COOH) and highest for pyromellitic acid with six COOH. Whether this behaviour was related simply to the number of COOH groups or to their increased acidity was not established. Where phenolic groups were also present, adsorption rose when the phenolic groups were in adjacent positions on the benzene ring and fell when these groups were adjacent to the COOH groups. Modelling the data (two layer model) required more than one type of surface species for each compound (six for pyromellitic acid).

The adsorption behaviour of 1,2,4,5-tetra carboxylic and 2,3-dihydroxybenzoic acids most closely simulated that of NOM (Evanko and Dzombak, 1998). Another modelling study, this time with CD-MUSIC, suggested that adsorption of carboxylic acids on goethite involved two complexes located on different crystal planes, viz. a deprotonated outer sphere complex (pH 3–9) and an inner sphere mononuclear chelate present at ca. pH 6 (Boily et al., 2000).

Most organics with double aromatic rings show maximum adsorption on goethite at low pH. The exceptions are cathecol and dihydroxynaphthalene, the adsorption of both of which rises as the pH rises from 3 to 8. Under alkaline conditions, both organics form strong surface complexes which appear to involve hydrogen bonding.

In acidic media, the extent of adsorption of para-substituted benzoic acid on ferrihydrite and goethite depends on the nature of the substituent (Kung and McBride, 1989). Adsorption decreases in the order:

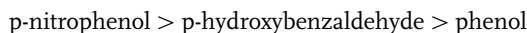
amino > methoxy > methyl > nitro

The different substituents have different electron donating/accepting properties and hence affect electron density and the acidity of the carboxyl group through which adsorption takes place. Electron accepting groups on the aromatic ring weaken the carboxylate-oxide surface bond.

Phosphonates adsorb on goethite up to a pH of 12, although like carboxylic acids, maximum adsorption is at low pH. The extent of adsorption rises as the number of phosphonate groups increases from one to five. Nitrilo trimethylene phosphonic acid (NTMP) adsorbs on goethite within minutes at pH 7. Complete desorption is effected at pH 12 after a number of hours. Equimolar amounts of Ca $^{2+}$ promote uptake of NTMP on goethite (Nowack and Stone, 1999).

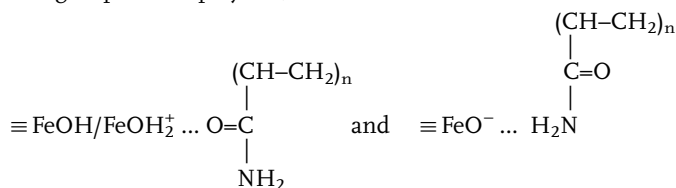
ATR-FTIR data indicated that on goethite, glycerophosphate adsorbs mainly as an inner-sphere, monodentate complex via the phosphonate group; the carboxylate group does not appear to be involved in surface coordination in this case (Sheals et al., 2002).

Evanko and Dzombak (1998) report that *phenol* does not adsorb on goethite which contrasts with the findings of McBride and Kung (1991) who found limited adsorption on ferrihydrite as well. The latter authors reported that substituted phenols adsorb on ferrihydrite and goethite in acidic media in the order:



Adsorption from solution is low ($0.005 \mu\text{mol m}^{-2}$ on ferrihydrite), but is far greater from the vapour phase, apparently because there is less competition with water for adsorption sites on the oxide (McBride & Kung, 1991). Steric hindrance due to the bulky methyl groups appears to be responsible for the negligible adsorption of 2–6 methyl phenol on goethite. Orthodiphenolic compounds form strongly adsorbing, chelating complexes on iron oxides (McBride, 1987).

The adsorption isotherm of *polyacrylamide*, a nonionic polymer, on hematite showed a steep rise at low solute concentrations followed by a shallower increase at high solute concentrations (Lee and Somasundaran, 1989). This can be interpreted as high affinity behaviour at low concentrations. Adsorption decreases slightly between pH 3.5 and 11.5. The adsorbed polymer did not affect the iep of hematite but did reduce the electrophoretic mobility and surface charge. Adsorption mainly involved hydrogen bonding through the carboxyl groups and, to a lesser extent, the amino groups of the polymer, i.e.



The high adsorption at low pH was correlated with the density of neutral and positive sites which hydrogen-bond to the carboxyl groups of the polymer. A second factor promoting adsorption was the comparatively low energy of solvation ($G_{\text{solv}} = 1.8 \cdot 10^{-3} \text{ kJ mol}^{-1}$). The marked decrease in adsorption above pH 10 was attributed to hydrolysis at high pH, of the polymer to a species which adsorbed less readily.

The surfactant *sodium dodecyl sulphate* ($\text{C}_{12}\text{H}_{25}\text{SO}_3\text{Na}$) and its sulphate adsorb electrostatically on hematite at low solute concentrations (Han et al., 1973). Hydrophobic effects operate at high concentrations due to the incompatibility of the hydrocarbon part of the molecule with water. This involves condensation of the alkyl chains at the surface (hemi-micelle interactions), which lowers the free energy of the system and reverses the surface charge.

Lauric acid ($\text{C}_{11}\text{H}_{22}\text{COOH}$) and *oleic acid* ($\text{C}_{17}\text{H}_{33}\text{COO}$) adsorb specifically on hematite at low solute concentrations; at high enough concentrations hydrophobic ef-

fects are also involved (Han et al., 1973). *Potassium octyl hydroxymate* adsorbs specifically on hematite at a level of $5 \cdot 10^{-4}$ M and shifts the iep from 8.5 to 6.0 at all concentrations (Han et al., 1973). There is some conflict in the literature concerning the behaviour of these surfactants upon adsorption (Shergold and Mellgren, 1971; Han et al., 1973). The inconsistency may be due to changes in speciation during the course of the experiment, either as a result of hydrolysis (of the alkyl sulphate and sulphonate), or due to decomposition with time (oleic acid).

The maximum adsorption (deposition) of three *proteins* on rhombohedral hematite ($SA = 19 \text{ m}^2 \text{ g}^{-1}$) ranged from 5 to 20 mg m^{-2} (Johnson and Matijevic, 1992a), and, for ovalbumin and γ -globuline occurred near their iep: 4.7 and 6.8, respectively. For lysozyme, however, the highest adsorption occurred at pH 9, much below its iep (11.0) and was probably due to strong intermolecular association of the protein (minimum solubility) at this pH. Protein uptake may depend on the number and kind of amino acids in the protein as well as on their association and conformational behaviour.

Maximum adsorption of *sodium octylbenzene sulphonate* on maghemite occurs at close to the critical micelle concentration (cmc) of the surfactant. This behaviour was attributed to complexation of the adsorbate with small amounts of Fe^{III} which had dissolved (Dao et al., 1998). On hematite, adsorption requires only a few seconds: high levels of the surfactant cause reversal of charge (at pH 4) from positive to negative (Zelenev & Matijevic, 1997). *Betamethasone phosphate* adsorbs on hematite via the phosphate groups of the adsorbate and lowers the iep of the oxide to below pH 3 (Vera et al., 1997). At temperatures below freezing, *styrene* forms a chemisorbed monolayer on magnetite and a physisorbed layer on the (111) plane of FeO (Wuhn et al., 2000). Adsorption of hydroxypyridines, quinolines and pyrimidines on hematite is only significant when the keto-enol (oxo-hydroxy) tautomeric equilibrium in aqueous solution favours the hydroxy tautomer (Vasudevan et al., 2001).

For natural surface systems, such as waters and soils, the interaction (adsorption) of dissolved, *natural organic (humic) material* (NOM) with Fe oxides has initiated much research (cf. Review by Piccolo et al., 1996), due, among other things, to its environmental relevance (Chap. 21). Fe oxides in soils are important adsorbents for humic compounds. This can be seen from the fact that soil horizons relatively rich in Fe oxides such as the B horizon of podsoils arrest humics migration down the profile. Conversely, removal of Fe oxides leads to a drastic drop in the retention of humics (Kaiser & Zech, 2000). Another aspect is the change in the adsorption of toxic chemicals by Fe oxides when humics cover the surface and modify the surface charge (Tipping & Cooke, 1982). In particular, enhanced adsorption of U^{IV} (Payne et al., 1996; Lenhard & Honeyman, 1999), Cu (Alcacio et al., 2001) and hydrocarbons (carbazole, anthracene and dibenzothiophene; Murphy et al., 1992) has been reported. Furthermore, adsorption of NOM on Fe oxides adds substantially to the stability of NOM against enzymatic oxidation to CO_2 in soils (Kaiser & Guggenberger, 2000) and sediments (Keil et al., 1994) and thus affects the global carbon balance.

Since humic equivalents for the experiments described below can not be synthesized, they must be extracted either from natural waters or soils. Two standards, viz.

the one from the Suwannee River (SR) and from the Great Dismal Swamp (GDS) waters and extractions from humiferous soil surface horizons (mostly podzols), peat or lignite are in use. Common extraction media are either water (dissolved organic carbon or matter; DOC, DOM) or alkali. The humics in the alkali extract are usually separated into an acid soluble (*fulvic acid*) and acid insoluble (*humic acid*) fraction. A humic acid standard is available at the International Humic Substance Society (IHSS) and also commercially (Aldrich humic acid).

Chemically, all these reference materials are mixtures of well defined single molecules and a large range of organic compounds with varying characteristics which are difficult to describe accurately. They are usually characterized by bulk properties, such as C and N content, total acidity, hydrophobicity/-phylicity (as defined operationally) and molecular size and weight, and structurally using various chemical and spectrographic (IR, NMR) methods, respectively. All these materials have been used for adsorption studies with Fe oxides.

In an early study, Tipping (1981), using aquatic NOM observed Langmuirian adsorption by goethite, hematite and 2-line-ferrihydrite with a saturation capacity at pH ~ 7 of ca 10; 20–40; and 150–225 mg humics g⁻¹ for hematite, goethite and non-aged and aged ferrihydrite, respectively. He also observed that the presence of low concentrations of Ca²⁺ and Mg²⁺ which are usually present in many surface waters, nearly doubled the adsorption, with the cations being coadsorbed.

Generally, as for simple organic acids and due to its acidic character, adsorption of NOM on Fe oxides increases with decreasing pH. Soil fulvic and humic acids from a podsol were adsorbed by goethite through the singly coordinated hydroxyl groups at around 100 mg g⁻¹ of solid (Parfitt et al., 1977a). The amount of podsol DOC adsorbed by goethite (SA 136 m²g⁻¹) was up to 2.5 $\mu\text{mol C m}^{-2}$ and at an addition of up to 500 $\mu\text{mol C}$ added per g of goethite it was completely adsorbed and linearly related to the solution concentration (Kaiser & Zech, 2000a). The DOC retained could be increasingly desorbed by water < sulphate $\ll$ phosphate (all at pH 5.3) < 0.1 M NaOH with the hydrophylic fraction being more easily extracted than the hydrophobic one (Fig. 11.5). Hysteresis increased with time and surface coverage. Between pH 4 and 9, desorption increased exponentially from 0 to 90% (Kaiser & Zech, 1999). SR-NOM was preferentially adsorbed over polyacrylic, phthalic and salicylic acid by hematite (Gu et al., 1996).

In another study, maximum adsorption of fulvic acid from a podzol B horizon by goethite was found to lie at ca. 0.6; 0.3 and 0.05 mg m⁻² at pH 4; 7 and 10, respectively and this was successfully described with the CD-MUSIC model (Filius et al., 2000). At low pH, binding involved inner sphere coordination with the carboxylic groups of the fulvic acid and, at high pH, outer-sphere coordination. In contrast to COOH groups, the N-containing functional (amino) groups of podsol-NOM do not appear to participate in the adsorption (Kaiser & Zech, 2000). As seen from DRIFT and NMR spectra of the non-adsorbed fraction of soil DOM, Fe oxides usually fractionate mixtures of their organic compounds. There is a general trend for preferential adsorption of the aromatic vs aliphatic, hydrophobic vs. hydrophylic – the former had a higher COOH-acidity – and bigger vs. smaller moieties. This was found for soil DOM (Murphy et al., 1992; Kaiser & Zech, 1997, 1998, 1999, 2000; Meier

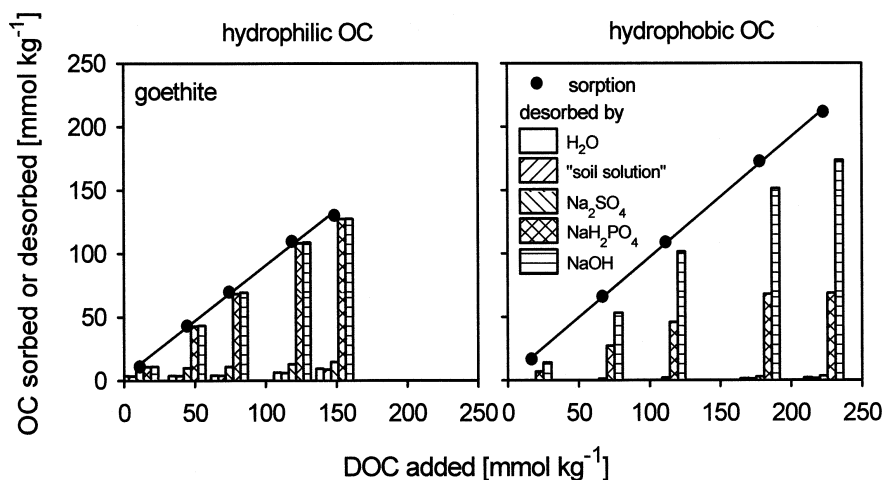


Fig. 11.5 Adsorption of DOC from a podsol by goethite and desorption after 24 hr of the hydrophilic and hydrophobic fractionation by different solutions. "Soil solution" was a DOC-free solution of similar inorganic composition as the DOC used for adsorption (Kaiser & Zech, 1999; with permission).

et al., 1999; Choreover & Amistadi, 2001) and for aquatic NOM (LiLi et al., 1997; Zhou et al., 2001). The adsorption affected the colloidal properties of the Fe oxide and caused displacement of nano-hematite particles attached to quartz grains in a column (Gu et al., 1996a). Both SR and GDS NOMs were adsorbed much more strongly on goethite than on kaolinite (Meier et al., 1999), but similarly on montmorillonite (Choreover & Amistadi, 2001). AFM pictures of an aquatic NOM on hematite were obtained by Namjesnik-Dejanovic and Maurice (2000).

Avena and Koopal (1999) used reflectometry to study the kinetics of adsorption of Aldrich humic acid on hematite. Uptake was fast (diffusion-controlled) at low pH, but slow at pH > 5. The rate of uptake rose with ionic strength above the iep, but decreased with ionic strength below the iep. The adsorption of humic acid onto hematite rendered its surface hydrophobic and made it a suitable sorbent for hydrophobic organic compounds (Murphy et al., 1992).

Bjorklund et al. (2001) showed with ellipsometry that fulvic acid adsorbed on a thin Fe^{III} oxide film (on an Fe substrate) could be photodesorbed into aqueous solution upon illumination with light of wavelengths up to 546 nm.

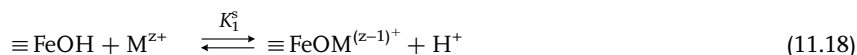
11.4

Cation Adsorption

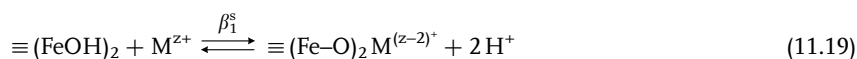
11.4.1

General

Adsorption of cations on iron oxides (Table 11.3) may be specific or non specific. With non specific adsorption, there is at least one water molecule between the adsorbing species and the surface functional group. *Specific* adsorption involves interaction with deprotonated surface hydroxyl groups to form mono- and bi-nuclear, inner sphere complexes, i.e.



and



with

$$K_1^s = \frac{\{\equiv \text{FeOM}^{(z-1)+}\} [\text{H}^+]}{\{\equiv \text{FeOH}\} [\text{M}^{z+}]} \quad (11.20)$$

$$\beta_1^s = \frac{\{\equiv (\text{FeO})_2 \text{M}^{(z-2)+}\} [\text{H}^+]^2}{\{\equiv \text{FeOH}\}^2 [\text{M}^{z+}]} \quad (11.21)$$

where K_1^s and β_1^s are the appropriate equilibrium constants. The surface speciation is generally determined on the basis of the measured extent of adsorption or from

Tab. 11.3 Cation adsorption studies on iron oxides.

Oxide	Cation	Reference
Goethite	Ag	78
	Al	54
	Au	8, 55, 83
	Cd	13, 22, 28, 30, 35, 44, 53, 57, 73, 74, 84, 92, 96
	Co	19, 27, 28, 33, 82, 89
	Cr	14
	Cu	11, 19, 28, 33, 71, 75, 76, 78, 89
	Hg	6, 16, 27, 36
	Mg	9
	Mn	9, 19, 33, 89
	Ni	13, 19, 30, 78, 89, 94
	Np	18
	Pb	5, 19, 28, 38, 39, 56, 62, 75, 77, 78
	Sr	15, 80
	U	41, 56, 61
	Zn	4, 5, 12, 13, 28, 30, 33, 72, 75, 78, 89, 95

Tab. 11.3 (continued)

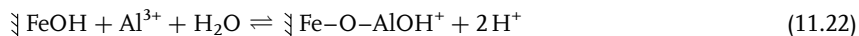
<i>Oxide</i>	<i>Cation</i>	<i>Reference</i>
Lepidocrocite	Al	99
	Cd	57, 74
	Fe	99
	Mn	86
	U	34, 61
	Zn	88
Akaganéite	Co	45
	Cd	74
	Mn	45
	Ni	45
	Zn	45
Ferrihydrite	Ag	68
	Ca	49, 51
	Cd	1, 7, 24, 25
	Co	1, 31, 46
	Cr	20, 81
	Cs	68
	Cu	7, 43, 60, 87, 93
	Eu	66, 68
	Ga	64
	Hg	50
	Lu	21
	Mn	46
	Ni	20, 46, 94
	Np	32
	Pb	1, 7, 69, 86, 93
	Rb	68
	Sr	3, 49
	U	17, 97
	Zn	7, 20, 31, 37, 42, 46, 51, 95, 98
Hematite	Ag	42, 78
	Al	42
	Au	47
	Ba	70
	Cd	26
	Co	2, 29, 65, 78
	Cr	68
	Cs	68
	Cu	29, 42, 78, 85
	Eu	66
	Fe	23
	Ga	67
	La	58
	Mn	68
	Ni	29, 78
	Np	52
	Pb	78
	Rb	68

Tab. 11.3 (continued)

<i>Oxide</i>	<i>Cation</i>	<i>Reference</i>
Magnetite	Sr	48, 68
	Th	63
	U	40, 63
	Zn	77, 78
	Ag	68
	Cd	68
	Co	10, 90, 91
	Cr	68
	Cs	59, 68
	Mn	68
	Ni	59
	Rb	68
	Sr	68
	Yb	59
	Zn	68, 88
Schwertmannite	Cd	74
	Cu	93
	Pb	93

Cation references; 1) Ainsworth et al., 1994; 2) Ambe et al., 1986; 3) Axe & Anderson, 1995; 4) Bar Yosef et al., 1995; 5) Barrow et al., 1981; 6) Barrow & Cox, 1992; 7) Benjamin & Leckie, 1981; 8) Berrodier et al., 1999; 9) Bleam & McBride, 1985; 10) Blesa et al., 1982; 11) Bochatay et al., 1997; 12) Bolland et al., 1977; 13) Brümmer et al., 1988; 14) Charlet & Manceau, 1992; 15) Collins et al., 1998; 16) Collins et al., 1999; 17) Combes, 1988; 18) Combes et al., 1992; 19) Coughlin & Stone, 1995; 20) Crawford et al., 1993; 21) Dardenne et al., 2001; 22) Davis & Upadhyaya, 1996; 23) Dempsey et al., 2002; 24) Dzombak & Morel, 1986; 25) Fendorf & Fendorf, 1996; 26) Fokkink et al., 1990; 27) Forbes et al., 1974; 28) Forbes et al., 1976; 29) Feuerstenau & Osseo-Assare, 1987; 30) Gerth & Brümmer, 1983; 31) Ghonemy et al., 1997; 32) Girvin et al., 1991; 33) Grimme, 1968; 34) Gueniot et al., 1982; 35) Gunneriusson, 1994; 36) Gunneriusson & Sjöberg, 1993; 37) Harvey & Linton, 1984; 38) Hayes & Leckie, 1986; 39) Hildebrand & Blum, 1974; 40) Ho & Doer, 1985; 41) Hsi & Langmuir, 1985; 42) Idzikowski, 1973; 43) Johnson, 1986; 44) Johnson, 1990; 45) Kanungo, 1994; 46) Kanungo, 1994a; 47) Karasoyova et al., 1998; 48) Karasoyova, 1999; 49) Kinniburgh et al., 1975, 1976; 50) Kinniburgh & Jackson, 1982; 51) Kinniburgh, 1983; 52) Kohler et al., 1999; 53) Kooner et al., 1995; 54) Lovgren et al., 1990; 55) Machesky et al., 1991; 56) Manceau et al., 1992; 57) Manceau et al., 2000; 58) Marmier et al., 1993; 59) Marmier et al., 1999; 60) McClaren & Crawford, 1974; 61) Moyes et al., 2000; 62) Muller & Sigg, 1992; 63) Murphy et al., 1999; 64) Music & Wolf, 1979; 65) Music et al., 1979; 66) Music & Wolf, 1979a; 67) Music & Wolf, 1979b; 68) Music & Rustic, 1988; 69) Nelson et al., 2000; 70) Nechaev & Sheir, 1979; 71) Padmanabham, 1989a; 72) Peneva & Paskaleva, 1981; 73) Petersen et al., 1993; 74) Randal et al., 1999; 75) Rhodda et al., 1993; 76) Roberson & Leckie, 1998; 77) Roe et al., 1991; 78) Rose & Bianchi-Mosquera, 1993; 79) Rueda et al., 1981; 80) Shai et al., 2000; 81) Sass & Raj, 1987; 82) Schenck et al., 1983; 83) Schoonen & Fisher, 1992; 84) Spadini et al., 1994; 85) Subramium & Yiacoumi, 2001; 86) Sung & Morgan, 1981; 87) Swallow et al., 1980; 88) Takai & Kozawa, 1976; 89) Yakematsu, 1979; 90) Tamura et al., 1983; 91) Tewari et al., 1972; 92) Theis et al., 1988; 93) Tonkin et al., 2002; 94) Trevedi & Axe, 2001; 95) Trevedi et al., 2001; 96) Venema et al., 1996; 97) Waite et al., 1994; 98) Xue & Huang, 1995; 99) Zhang et al., 1992.

modelling, rather than directly from spectroscopic data. Trivalent cations appear to adsorb as surface hydroxo species, i.e.



Cation adsorption is accompanied by release of protons with the number of protons released per cation being termed z . Ideally, z should be one for mononuclear complexes and two for binuclear complexes, but in fact, the value is often found to be between one and two. In addition, the value of z may also vary between these limits as the pH rises. The occurrence of intermediate values has been attributed to the simultaneous formation of binuclear complexes and mononuclear species and to the presence of different surface sites (Hohl & Stumm, 1976; Benjamin & Leckie, 1891; Schindler, 1984).

Cation adsorption may be suppressed as the ionic strength increases and this is usually considered to indicate outer sphere (non specific) adsorption, although it may also be the result of ion pairing in solution. There are reports that increasing the ionic strength in some cases increases cation uptake on Fe oxides, possibly due to more effective shielding of the highly charged, surface complexes (Venema et al., 1996; Lutzkirchen, 1997). Crisenti and Svenjensky (1999) showed that the effect of ionic strength on cation adsorption on iron oxides depends upon the nature of the electrolyte. Increased adsorption of cations with rising ionic strength has been observed in NaClO_4 solutions. In NaNO_3 solution, ionic strength has no effect upon adsorption of transition and heavy metal ions, but increased ionic strength depresses adsorption of alkaline earth ions. Although data for NaCl solutions is limited, it appears that in such solutions, adsorption of alkaline earth, transition and heavy metal ions falls with rising ionic strength. In view of these observations, dependence of adsorption on ionic strength cannot be considered a reliable indicator of outer sphere adsorption.

A plot of cation adsorption versus pH is sigmoidal (Figure 11.6). Adsorption increases from 0 to 100% of the total uptake over a narrow region, usually covering 1–2 pH units, termed the adsorption edge. The pH at which half of the total adsorption has occurred (pH_{50}) decreases as the first hydrolysis constant of the metal ion in solution rises. This observation was interpreted by some workers as indicating that the hydrolysed metal ion adsorbs in preference to the unhydrolysed species. The surface complexation approach removes the need to invoke hydrolysed species because surface complexation equilibria and the hydrolysis/adsorption sequence are indistinguishable. The correlation between the first hydrolysis constant of the metal in solution and the amount adsorbed by the oxide simply reflects the affinity of the metal for the surface OH groups of the oxide.

The higher the pH of the adsorption edge, the weaker is the resulting metal-surface complex. The strength of first row transition metal ion adsorption on goethite is $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$: the same order is followed for hematite except that the positions of Cu and Pb are reversed (Grimme, 1968; McKenzie, 1980; Gerth and Brümmer, 1983). On ferrihydrite, the order is $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Ca}$ (Dzombak and Morel, 1990). The order of cation affinity for goethite has

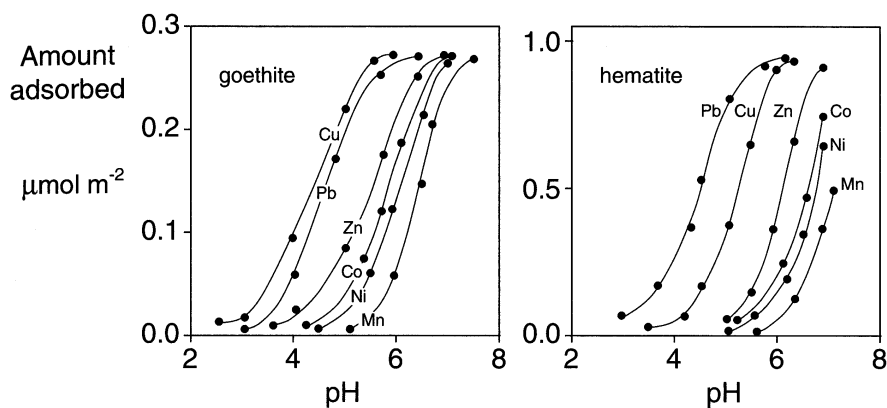


Fig. 11.6 The effect of pH on the adsorption of some heavy metal cations on goethite and hematite, showing the typical adsorption edge for heavy metals (McKenzie, 1980, with permission).

been shown to depend on the temperature of the system and on the time allowed for adsorption (Brümmer et al., 1988): the same may apply to other Fe oxides in which case, differences in experimental conditions may account for the differences in order of affinity. The adsorption edges of cations on Fe oxides shift to a higher pH as the initial concentration of the ion in solution rises and as the solid/solution ratio falls (Benjamin and Leckie, 1981; Brümmer et al., 1988). On the other hand, the adsorption edges of Zn, Cu, Pb and Cd on goethite shifted to lower pH values as the temperature of the system rose from 10 to 70 °C (Johnson, 1990; Rhodda et al., 1993). In other words, increasing the temperature appears to promote cation adsorption (Macheský, 1985).

Cation adsorption on Fe oxides is initially rapid, but adsorption of trace metals can continue to increase over days with long reaction times being needed to reach equilibrium. Adsorption of Ni, Zn and Cd on goethite rose as the reaction time was extended from 2 hr to 42 days (Brümmer et al., 1988). It was suggested that the process involved rapid adsorption on the external surfaces of the crystals followed by slow diffusion into the particles, possibly along the domain boundaries, with finally, adsorption on internal sites. Data from the slow stage was fitted to a diffusion model (Barrow et al., 1989). Slow adsorption of Sr on ferrihydrite has been attributed to intra-aggregate diffusion (Axe and Anderson, 1995). More Cu and Pb was adsorbed during the slow stage of adsorption on ferrihydrite that had been freeze dried, than on the material in suspension (Figure 11.7) (Scheinost et al., 2001). Whether adsorption of cations is reversible depends both on the metal and on the type of surface complex that forms. Lead desorbs completely from goethite (Padmanabham, 1983), whereas Cu, Zn, Cd, Ni and Co display hysteresis (Padmanabham, 1983; Brümmer et al., 1988; Barrow et al., 1993). The difficulty of desorbing cations from Fe oxides has been attributed to the formation of inert surface complexes (Quirk and Posner, 1975).

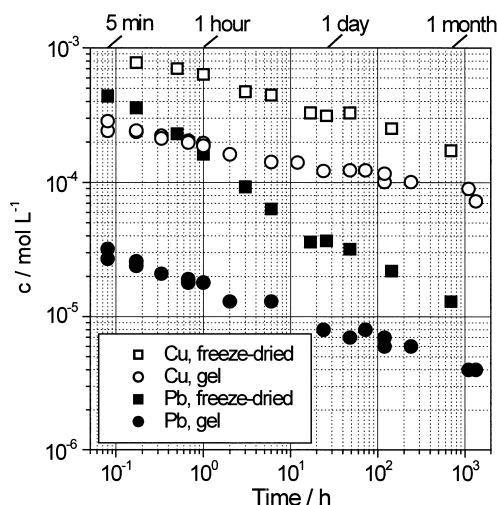


Fig. 11.7 Kinetics of Cu and Pb removal from solution by a freeze-dried (■) and an undried (gel) (□) of 2-line ferrihydrite at 24 °C (Courtesy A. Scheinost; see also Scheinost et al., 2001; with permission).

11.4.2

Examples of Cations

Adsorption of **aluminium** on Fe oxides is of interest in view of the fact that Al is the most important substituting ion in goethite (see Chap. 3) and also because of the environmental effect of high levels of Al in acidic, natural waters and soils. Adsorption on goethite takes place over the pH range 3–8.5 and has been modelled using the constant capacitance model (Lovgren et al., 1990; Lovgren, 1991). The best fit to the adsorption data was obtained with two monodentate surface hydroxo-complexes – FeOAlOH^+ and $\text{FeOAl}(\text{OH})_2$ – which formed successively as the pH rose. Desorption of Al from goethite is extremely slow and adsorption is only partly reversible. It has been suggested that the strong affinity of Al for the goethite surface may be the first step in the formation of an Al substituted goethite (Lovgren et al., 1990). On lepidocrocite, Al adsorbs over the pH range 3–5.5 (Fig. 11.8) and forms two surface hydroxo complexes similar to those postulated for goethite and with similar stability constants (Zhang et al., 1992). The Al complexes on both Fe oxides appear to be very stable.

Divalent **iron** adsorbs on lepidocrocite over the pH range 5–7 (Fig. 11.8) and modelling of the adsorption data indicated that the most likely surface complexes to form are $\equiv \text{Fe}-\text{O}-\text{Fe}^+$ and a hydroxo species, $\equiv \text{FeOFe}(\text{OH})$ (Zhang et al., 1992). The stability constants for these species (Table 11.4), together with the higher pH of adsorption, indicate that Fe^{2+} adsorbs less strongly on lepidocrocite than does Al^{3+} . Under anoxic conditions, adsorption of Fe^{2+} at pH > 4 on hematite involved a two stage process with the second, slow stage consisting of adsorption followed by surface precipitation (Dempsey et al., 2001). The authors suggested that this behaviour was consistent with the aut precipitation of magnetite.

The **alkaline earth ions** have fairly diffuse adsorption edges which cover a wide pH range, e.g. 7–11.5 for Ca^{2+} (Ali and Dzombak, 1996) and 7–11 for Sr^{2+} on

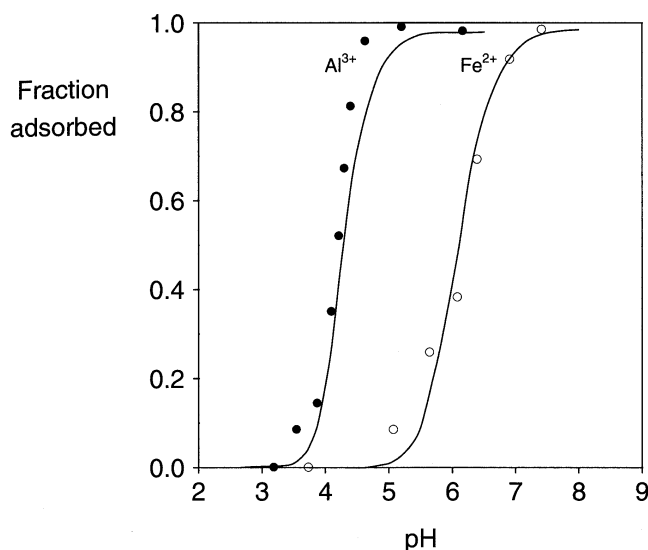


Fig. 11.8 Adsorption of Al^{3+} and Fe^{2+} on lepidocrocite as a function of pH (Zhang et al., 1992, with permission).

Tab. 11.4 Intrinsic stability constants and proposed surface complexes for cations adsorbed on iron oxides.

Oxide	Cation	Surface complex	Stability constant	Reference
Goethite	Al^{3+}	$\equiv \text{FeOAlOH}^+$	$\log K_{\text{int}}^1 = -1.49$	Lovgren et al., 1990
		$\equiv \text{FeOAl}(\text{OH})_2^0$	$\log \beta = -9.10$	
		constant capacitance model		
	Cd^{2+}	$\equiv \text{FeOCd}^{2+}$	$\log K_{\text{int}}^1 = -6.0$	Benjamin, 1978
		$\equiv \text{FeOCdOH}^+$	$\log K_{\text{int}}^2 = -9.3$	
		triple layer model		
Lepidocrocite	Pb^{2+}	$\equiv \text{FeOPb}^+$	$\log K_1^s = -0.52$	Müller and Sigg, 1992
		$(\equiv \text{FeO})_2\text{Pb}$	$\log \beta_2^s = -6.27$	
		diffuse layer model		
	Mn^{2+}	$\equiv \text{FeOMn}^+$	$\log K = -6.1$	Davies and Morgan, 1989
		$(\equiv \text{FeO})_2\text{Mn}$	$\log \beta = -12.7$	
	Al^{3+}	$\equiv \text{FeOAlOH}^+$	$\log K = -2.74$	Zhang et al., 1992
		$\equiv \text{FeOAl}(\text{OH})_2^0$	$\log \beta = -9.53$	
		constant capacitance model		
	Fe^{2+}	$\equiv \text{FeOFe}^+$	$\log K = -8.53$	Zhang et al., 1992
		$\equiv \text{FeOFe}(\text{OH})^0$	$\log \beta = -2.13$	
		constant capacitance model		

goethite and hematite (Karasyova et al., 1999). Adsorption of Sr has attracted interest because this element is a carcinogenic and extremely mobile nuclide which is released from low level, radioactive waste and may be immobilised by adsorption on soil Fe oxides. EXAFS data suggests that at pH 8.6 and under atmospheric conditions, Sr precipitated on goethite as strontianite (SrCO_3) with uptake being promoted by increased P_{CO_2} (Sahai et al., 2000): at higher pHs, a surface complex rather than a precipitate formed. Other EXAFS data also supported formation of a surface complex at higher pH viz an outer sphere complex at pH 9.2 and an inner sphere bridging, bidentate surface complex at pH 10.2 (Collins et al., 1998). Karasoyova et al. (1999) concluded, on the basis of titration data obtained under a CO_2 free atmosphere and modelled with the constant capacitance model, that Sr adsorbed on hematite to form monodentate, inner sphere complexes. Adsorption of Sr on both hematite and ferrihydrite rose as the temperature increased from 25 to 75 °C.

Chromium adsorbs as the cation (Cr^{3+}) over the pH range 2.5–4 on ferrihydrite and goethite (Charlet and Manceau, 1992; Crawford et al., 1993): it is less toxic in the trivalent than in the hexavalent state. Adsorption of low levels (10^{-5} M) of chromium follows a Langmuir isotherm and can be modelled with a single, inner sphere complex. At higher concentrations of Cr, there was a transition from adsorption to surface precipitation (Figure 11.9) (Farley et al., 1985; Manceau et al., 1992). There is controversy about the structure of the surface precipitate. EXAFS suggested that the adsorbed species are grouped in multinuclear clusters (Fig. 11.9b) which have the lepidocrocite structure (Manceau et al., 1992), whereas scanning force microscopy appeared to show that the precipitate is distributed as a coating over the entire goethite surface (Fendorf et al., 1996).

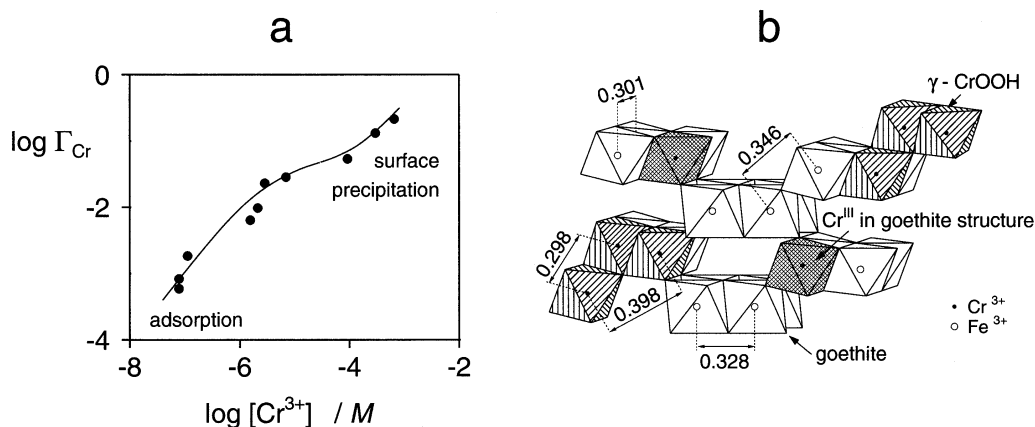


Fig. 11.9 a) Retention of Cr^{III} by goethite; Γ_{Cr} (unitless) vs. Cr^{III} equilibrium concentration showing the transition from adsorption to surface precipitation. b) Structural model of incorporated and adsorbed Cr^{III} by goethite (Charlet & Manceau, 1992, with permission).

Adsorption of Zn, Cd and Hg (the IIB elements) on Fe oxides has been studied intensively because these three elements are common, toxic pollutants of soils and waters. Adsorption of **mercury** on goethite is less extensive and starts at a lower pH than does that of the other two elements. The adsorption edge is between pH 3–5 and at higher pHs Hg desorbs to form the stable and soluble $\text{Hg}(\text{OH})_2^0$ species (Gunneriusson and Sjöberg, 1993). EXAFS data suggest that on goethite, Hg adsorbs at the edge sites on {101} as a binuclear complex (Collins et al., 1999). On Fe oxides, the adsorption edge of cadmium extends from around pH 6 up to pH 10 (Hoins et al., 1993; Hooner et al., 1995; Sparks et al., 1995; Randall et al., 1999) and shifts to higher values with rising temperature (Johnson, 1990). EXAFS showed that low levels of Cd adsorb on the {201} planes of goethite at edge sites, but with increasing adsorption, bidentate complexes linking Cd and two, corner sharing $\text{Fe}(\text{OH})_6$ octahedra on the {101} and {100} planes predominate (Fig. 11.3) (Spandini et al., 1994; Parkman et al., 1999). In fact, at high surface loadings, the edge complexes on the minor {201} planes make too small a contribution to the total for them to be detectable by EXAFS and this probably accounts for claims that only corner sharing complexes form (Randall et al., 1999; Manceau et al., 2000). Combined EXAFS and AFM studies of the different polymorphs of FeOOH suggest that the stacking arrangement of anions in the crystal structure strongly affects the type of Cd surface complex that forms (Manceau et al., 2000). In contrast to goethite, lepidocrocite has few or no corner sharing Cd surface complexes even at high loadings because the layer structure of lepidocrocite favours edge complexes (Fig. 11.3b). The type of complex that forms appears to be independent of pH and the degree of surface saturation. Cadmium adsorption on akaganéite and schwertmannite involves an inner sphere complex, the details of which have not yet been established (Randall et al., 1999). EXAFS data suggest that on goethite **zinc** (Schlegel et al., 1997) and also **copper** (Bochatay et al., 1997) adsorb as inner sphere complexes which display Jahn Teller distortion.

Adsorption of the **uranyl** ion (UO_2^{2+}) on Fe oxides is usually considered to involve inner sphere, probably bidentate, surface complexes (Hsi and Langmuir, 1985; Charlet and Manceau, 1992; Waite et al., 1994; Moyes et al., 2000). On hematite, there is a sharp adsorption edge between pH 4 and 5.5 and on goethite, the adsorption edge is at pH 5–6 (Liger et al., 1999; Lenhart and Honeyman, 1999). If carbonate is not excluded from the system, complexation with this anion depresses adsorption of U on Fe oxides although there is some spectroscopic evidence that ternary uranyl-carbonate surface complexes can form under certain conditions (Bargar et al., 2000). At pH 6, adsorption and desorption of uranyl on goethite is rapid being complete within minutes to hours (Giammar and Hering, 2001). Adsorption of **lanthanum** on goethite occurs up to around pH 5.5, but at pH 8 surface precipitation (shown by HRTEM) takes place (Fendorf and Fendorf, 1996). Modelling of adsorption data combined with EXAFS results suggested that **lutetium** adsorbs on ferrihydrite as a monodentate surface complex at low pH and a bidentate complex above pH 5.5 (Dardenne et al., 2001).

11.5

Adsorption from Mixed Systems (Table 11.5)

In systems containing two or more adsorbates, either *competitive* or *synergistic* effects may operate. The commonest synergistic effect is that of ternary adsorption (11.5.4). Competitive behaviour may involve competition for the same surface sites, indirect effects due to the change in the electrostatic properties of the oxide/water interface and in some cases, formation of non sorbing, metal-ligand complexes in solution.

Tab. 11.5 Adsorption of Competing Ions

<i>Oxide</i>	<i>Competing Ions</i>	<i>Reference</i>
Goethite	Phosphate/sulphate	Parfitt (1982)
	Phosphate/citrate	Geelhoed et al., 1998
	Phosphate/glucophosphonate	Gimsing & Borggaard, 2001
	Phosphate/oxalate or sulphate	Lui et al., 1999
	Phosphate/humics	Sibanda & Young, 1986
	Phosphate/O-phthallate	Nilsson et al., 1996
	Phthalate/sulphate	Ali & Dzombak, 1996
	Chelidamic acid/sulphate	
	Organic acids/sulphate/Cu	Ali & Dzombak, 1996a
	Phosphate/As(V)	Manning & Goldberg, 1996
	Phosphate/Mo	
	Phosphate/Zn	Bolland et al., 1977
	Cd/phosphate or sulphate or humate	Collins et al., 1999
	Cd/sulphate	Hoins et al., 1993
	Cd/phosphate	Venema et al., 1997
	Cd/humics	Davis & Bhatnagar, 1995
	Cd/oxalate	Lamy et al., 1991
	Cd/Sr	Cowan et al., 1991
	Hg/Cl	Barrow & Cox, 1992; Guneriusson & Sjoberg, 1993
	Phthalic or Chelidamic acid/Cu or Ca	Ali & Dzombak, 1996b
	Glycine/Cu	McBride, 1985
	Humic acid/Mg or Ca	Tipping, 1981
	Polyacrylate or polymethacrylate/M ^{II}	Vermohlen et al., 2000
	NOM/Cu or Cd or Ni	Buerger-Weirich et al., 2002
Hematite	U/humic acid	Lenhart & Honeyman, 1999
	Cu/Pb	Christl & Kretschmar, 1999
Lepidocrocite	Phosphate/Zn	Diaz-Barrientos et al., 1990
Ferrihydrite	Ni/EDTA	Ho & Miller, 1985
	Cd/phosphate	Benjamin & Bloom, 1981
	U/phosphate or humic acid	Payne et al., 1996
	Zn/phosphate	Ghanem & Miklesen, 1998
	Cu/Zn, Cd or Pb	Benjamin & Leckie, 1981a
	Pb/Cl, SO ₄ or S ₂ O ₃	Benjamin & Leckie, 1982
	Cu/picolinic acid	Davis & Leckie, 1978a

The actual extent of uptake of competing ions usually depends upon the proportions of the ions in the system (i.e. whether one is in excess) and on the order of addition to the system. *In situ* voltametry has recently been shown to be very useful for investigation of adsorption from mixtures of low levels (10^{-6} – 10^{-3} M) of metal ions (Palmquist et al., 1999).

11.5.1

Competition Between Anions

Phosphate suppresses adsorption of arsenate and selenite on goethite with the effect being greater the higher the concentration of phosphate (Hingston et al., 1971). It also causes desorption of arsenate and arsenite from goethite and ferrihydrite at pH 3 (Jackson & Miller, 2000). Phosphate also strongly promotes desorption of sulphate and to a lesser extent, oxalate, from goethite (Lui et al., 1999). It depressed citrate adsorption on goethite over a wide pH range, whereas citrate, conversely, only reduced phosphate uptake at pHs >7 (Geelhoed et al., 1998); this system was successfully modelled using the CD-MUSIC model with parameters obtained from single anion experiments. Adsorption of phosphate on ferrihydrite is suppressed by both citrate and tartrate (Earl et al., 1979) and this is believed to be the mechanism by which plant roots which excrete simple di- and tricarboxylic acids, mobilize adsorbed phosphate and improve their P supply (Gartener et al., 1982; Dinkelaker et al., 1989; Gerke et al., 1994). On the other hand, silicate, phosphate and carbonate suppressed the adsorption of mugineic acid on ferrihydrite and thus hindered the release of Fe (to plant roots) by siderophores (see Chap. 12) (Watanabe and Matsumoto, 1994). Phosphate desorbs silicate from goethite (Torrent et al., 1992). Both phosphate and silicate block cysteine (at tenfold lower concentrations) adsorption on ferrihydrite (Cornell & Schneider, 1989).

The practical significance of such competition evolves from the experience that silicate and (anionic) humics can increase the efficiency of phosphate fertiliser because these compounds occupy sites suitable for phosphate adsorption (Hingston et al., 1968; Schwertmann, 1995). Hydroxyl is another anion that competes effectively with adsorbing anions, owing to its location in the inner Helmholtz layer. The release of adsorbed phosphate after liming a soil or after inflow of acidic surface soil into weakly alkaline surface waters due to erosion, can be considered as the result of competition between OH^- and phosphate ions.

Chromate adsorption by iron oxides is suppressed by a large excess of carbonate or silicate species. Competition between silicate and borate adsorption on ferrihydrite was reported by McPhail et al. (1972). Low levels of sulphate suppress uptake of phthalic and chelidimic acids by goethite (Ali & Dzombak, 1996a).

11.5.2

Competition Between Cations

Competitive adsorption between different cations is most important when the concentrations of all cations are low and there is competition for the limited number

of high energy sites on the oxide (Benjamin & Leckie, 1981a). Zn suppresses the adsorption of Cd on ferrihydrite (Benjamin & Leckie, 1981a). Cd adsorption is also reduced by high levels of weakly adsorbing, alkaline earth ions (Balistrieri and Murray, 1982; Cowan et al., 1991). Equal concentrations of Zn and Ni adsorb independently of each other on ferrihydrite, but Cr^{3+} enhances the uptake of these metals (Crawford et al., 1993). It has been suggested that either mixed metal hydroxo surface species form or that the surface properties of the oxide have been altered by Cr adsorption.

Between pH 4.5–6.3, Pb strongly reduced adsorption of Cu on hematite, whereas the effect of Cu on Pb uptake was less pronounced when the concentrations of both cations were the same (Christl and Kretschmar, 1999). Palmquist et al. (1999) noted that uptake of Cu and Zn from equimolar solutions was additive.

11.5.3

Interactions Between Cations and Anions

The presence of chelidamic acid strongly reduced uptake of Ca on goethite especially at high pH, presumably due to the formation of solution complexes (Ali & Dzombak, 1996). Complexing ligands that are not strongly adsorbed by the oxide may hold the metal ion as a complex in solution; one example is the OH^- ion which, when in large excess (i.e. at high pH), holds the cation (e.g. Al) as a soluble complex. Analogously, adsorption of Ag on ferrihydrite was lowered by the formation of complexes with chloride and with cyanide ions and Cu adsorption on ferrihydrite was suppressed by picolinic acid (Davis and Leckie, 1978a). Excess of glycine and cysteine suppressed adsorption of Cu on hematite at high pH (Music et al., 1979). In the presence of carbonate, sorption of arsenic species on ferrihydrite is depressed (Appelo et al., 2002). Enhanced adsorption of Cd on goethite caused by the presence of sulphate or phosphate in the system was attributed to electrostatic effects, i.e. altered surface charge, whereas citrate and oxalate promoted Cd adsorption by forming a surface precipitate with the cation (Collins et al., 1996a). Adsorption of Cd on hematite was enhanced by the presence of humic acid (Davis and Bhatnagar, 1995). Coadsorption due to electrostatic effects was also reported for Sn and phosphate on lepidocrocite (Diaz-Barrientos et al., 1990) and for Zn and phosphate on ferrihydrite (Ghanem and Milkesen, 1998).

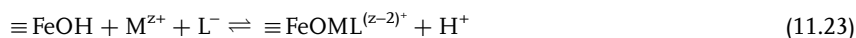
Rietra et al. (2001) measured the simultaneous adsorption of phosphate and calcium on goethite over the pH range 4–11 and modelled the data with the CD-MUSIC model. They concluded that the observed adsorption took place in response to electrostatic effects and that ternary adsorption was not involved.

11.5.4

Ternary Adsorption

The presence of anions in solution may enhance cation adsorption by formation of mixed metal/ligand surface complexes (Schindler, 1990). This effect is termed ternary adsorption. Two forms of ternary adsorption have been identified:

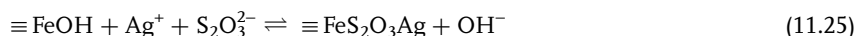
1. Coordination of the metal to the oxide surface and to the ligand, i. e.



2. The case where a polydentate ligand bridges the adsorbed metal ion and the surface metal ion, i. e.



To date, only the second form of ternary adsorption has been observed for iron oxides. Davis and Leckie (1978a) found that thiosulphate adsorbed on ferrihydrite in acid media with adsorption decreasing to zero as the pH rose to ca. 7, whereas the adsorption edge of silver lay between pH 7 and 8. In the presence of thiosulphate, adsorption of silver was enhanced in the pH range 4–6.5 (Fig. 10.10), i. e.



The effect increased with increasing concentration of thiosulphate. Above pH 7, thiosulphate suppressed adsorption of Ag^+ by holding the cation as a complex in solution. Adsorption of Ag^+ on ferrihydrite was also enhanced by glutamic acid and that of Cu^{2+} was promoted by both glutamic acid and by 2.3-pyrazidinedicarboxylic acid.

Trace metal adsorption on goethite is reportedly increased by the presence of sulphate ions (Balistrieri and Murray, 1982). Arsenate and antimony oxyanions enhance uptake of cobalt on ferrihydrite and hematite, respectively (Benjamin and Bloom,

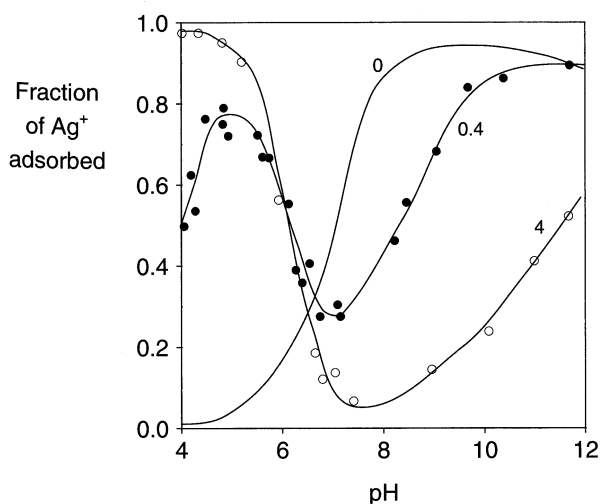


Fig. 11.10 Adsorption of Ag^+ on ferrihydrite as a function of pH and total thiosulphate concentration in the absence and presence of 0.4 and 4 $\mu\text{mol L}^{-1}$ thiosulphate (Davis & Leckie, 1978, with permission).

1981; Ambe et al., 1986) and phosphate adsorbed on lepidocrocite raised the adsorption of zinc (Madrid et al., 1991 a). Adsorption of Cd on goethite is increased by sulphate (Hoins et al., 1993) and by oxalate (Lamy et al., 1991).

The interaction of phosphate with Cl^- and Na^+ is shown in Figure 11.11. Upon adsorption of phosphate onto goethite, Cl^- adsorption dropped to zero, whereas adsorption of Na^+ increased substantially (Nanzyo and Watanabe, 1981, 1982). It was suggested that adsorption of phosphate is followed by adsorption of additional cations at $\text{pH} > 7$.

Above pH 5, chelidamic acid strongly and phthalic acid less so, enhance adsorption of Cu on goethite and shift the adsorption edge of the cation to lower pHs (Ali and Dzombak, 1996). Sulphate similarly enhances adsorption of Cu on goethite (Ali and Dzombak, 1996 b). Addition of sulphate to the Cu/chelidamic acid system dramatically lowered Cu adsorption on goethite. On the basis of modelling results, it was proposed that sulphate competed with the Cu-ligand complex for surface sites and in addition, adsorbed sulphate reduced the overall positive charge on the oxide which also hindered adsorption of the metal/ligand complex (Ali and Dzombak, 1996 b). ATR-FTIR data supports formation of ternary surface complexes on hematite in the hematite/Pb/malonic acid system (Lenhart et al., 2001).

Ternary adsorption of humic molecules and Ca^{2+} ions modified the surface charge and the colloidal behaviour of goethite (Tipping and Cooke, 1982). Fe oxides in natural environments often form in the presence of or through the activity of, micro-organisms (see Chap. 17). The adsorption properties of the oxides may, therefore, be modified by adsorbed organic molecules and ternary Fe-OCO-M complexes (CO-org.

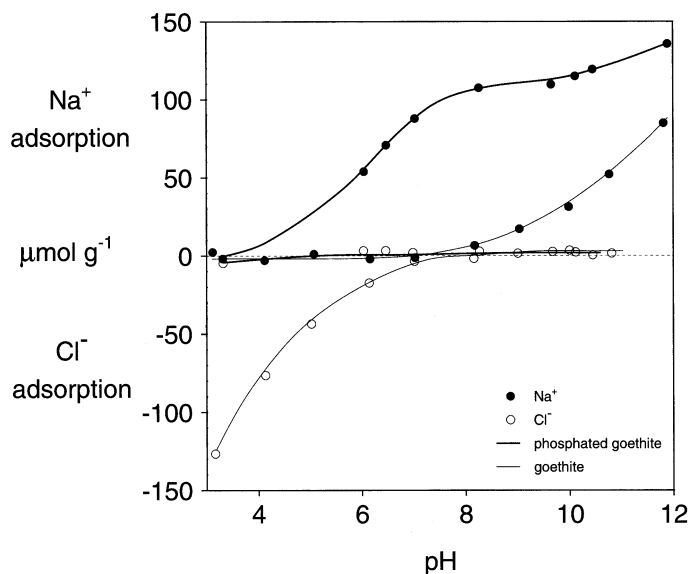


Fig. 11.11 Na^+ and Cl^- adsorption on pure and phosphated goethite (Nanzyo & Watanabe, 1982, with permission).

compound, M = metal) may form. For example, pH_{50} (p. 548) of Sr on ferrihydrite formed in the presence of *Shewanella* was at 5.5–5.9 in contrast to the pH_{50} of Sr on pure ferrihydrite. The maximum amount of adsorbed Sr fell from 0.079 mmol g^{-1} for the surface of the bacterium cell to 0.034 mmol g^{-1} for the bacterium/ferrihydrite composite indicating that ferrihydrite partly blocked adsorption sites on the cell surface (Small et al., 1999).

11.6

Adsorption of water

The role adsorbed water plays in dissolution/precipitation reactions, catalytic processes such as the water gas shift reaction and photocatalytic splitting of water on Fe oxide electrodes, has prompted various studies of the adsorption of water on Fe oxides. These studies were usually carried out under ultra high vacuum (UHV) on thin films of magnetite, hematite or FeO. Photoelectron and thermal desorption spectroscopy showed that at temperatures of between 235 and 140K, three types of adsorbed water, namely dissociatively chemisorbed, physisorbed monomeric and hydrogen bonded ice, could be identified on the magnetite (111) plane (Joseph et al., 1999). Dissociative chemisorption of water takes place on regular surfaces, but not at defect sites (Joseph et al., 1999a). Consecutive STM imaging has shown that the diffusion of adsorbed water on magnetite (111) involves both rotational and translational movement (Shackhutinov and Weiss, 2000). The heat of adsorption of water on magnetite is ca. 50 kJ mol^{-1} . On the FeO (111) plane, only physisorption of water occurred and this was attributed to the absence of exposed Fe sites at the oxide surface (Joseph et al., 1999a). The chemical reactivity of water to Fe oxide surfaces under UHV conditions appears to be related to the presence of the exposed Fe sites. Various techniques including ultra-violet photoelectron spectroscopy (UPS) and XPS (see Chap. 7) indicate that water does not adsorb strongly on the hematite (001) plane (Hendlewerk et al., 1986; Kurtz and Heinrich, 1987; Junta-Rosso and Hochella, 1996). For adsorption to occur on this plane, a water vapour pressure in excess of 10^{-4} Torr is required (Lui et al., 1998). SIMS and programmed thermal desorption studies showed that water adsorbs dissociatively on both the reconstructed (2x1) and the (1x1) hematite (021) plane to generate terminal and bridging hydroxyl groups (Henderson et al., 1998). Whether the surface was reconstructed or not affected the stability and reactivity of the adsorbed water.

11.7

Adsorption of gases (Table 11.6)

In general, the adsorption behaviour of gases on iron oxides has been investigated either because the gases are atmospheric pollutants (NO , SO_2 , CO_2), or because they act as probe molecules and provide information about surface sites. The adsorption sites on iron oxides are usually the Lewis acid sites.

Tab. 11.6 Adsorption studies of gases on iron oxides.

Oxide	Gas	Reference
Goethite	CO ₂	Russell et al., 1975
	SO ₂	Kaneko and Inouye, 1981
	pyridine, acetic acid vapour, CO ₂ , nitric oxide, trimethyl chlorosilane	Rochester and Topham, 1979c
	NO, SO ₂	Kaneko and Matsumoto, 1989
	NO, SO ₂ , CO ₂	Ishikawa and Inouye, 1983
	SO ₂	Inoue et al., 1988
Lepidocrocite	CCl ₄ , nC ₆ H ₁₄ , CH ₃ OH	Ishikawa et al., 1992a
Hematite	NH ₃ , H ₂ S, ETOH, ET ₂ OH, N ₂ , O ₂ , H ₂ , CO, SO ₂ , Cl ₂ , C ₂ H ₆ , C ₂ H ₄	Blyholder and Richardson, 1962
	NH ₃ , pyridine, nitric oxide, CO ₂ , acetic acid, vapour, trimethyl chlorosilane	Rochester and Topham, 1979b
	N ₂ , H ₂ O, CH ₃ OH, CCl ₄ , C ₆ H ₆ , C ₆ H ₅ Cl	Ishikawa et al., 1993

CO₂ is particularly strongly adsorbed from both the aqueous and the gaseous phase on goethite and, since it is omnipresent, it must be removed before undertaking surface or adsorption studies (see Chap. 10). The adsorption isotherm shows a steep rise at low CO₂ pressures, followed by a more gradual increase at higher pressures. Desorption is slow and the adsorption/desorption curves display marked hysteresis. Infrared studies indicate that CO₂ adsorbs strongly as CO₃²⁻ on moist goethite, and as both CO₃²⁻ and HCO₃ on the dry solid. The CO₃²⁻ surface complex is considered to involve coordination to a triply coordinated O²⁻ ion and, in addition, hydrogen bonding to two singly coordinated hydroxyl groups; this complex is extremely stable (Russell et al., 1975). On moist hematite, CO₂ adsorbs to form carboxylate, bicarbonate and carbonate species (Rochester and Topham, 1979b). During crystal growth, carbonate may even be incorporated into goethite, and can thus be used as a source of the stable carbon isotope to characterize the environment in which the goethite formed (Yapp, 1993; see Chap. 15).

Adsorption of NO on goethite followed a Langmuir isotherm. NO displaced previously adsorbed SO₂ and CO₂ from the surfaces of goethite, akaganéite and lepidocrocite, but was not itself displaced, i.e. it adsorbed more strongly than the other gases (Ishikawa and Inouye, 1983). Adsorption was initially rapid (hours) and proceeded subsequently more slowly (days) (Kaneko and Inouye, 1987). Infrared spectroscopy indicated that NO adsorbed initially on goethite to form nitro species, and upon further reaction formed either binuclear (bridging) or chelating nitrato species (Rochester and Topham, 1979c). On the basis of combined FTIR and *in situ* electrical conductivity measurements, mono- and bidentate nitrito and nitrosyl surface complexes have also been suggested (Kaneko and Matsumoto, 1989). Adsorbed NO caused changes in the electrical conductivity of goethite (Kaneko and Inouye, 1987). NO did not adsorb on hematite (Rochester and Topham, 1979b).

Adsorption of NH_3 on hematite followed a Langmuir isotherm and had a heat of adsorption of 48.3 kJ mol^{-1} (Blyholder and Richardson, 1962). Infrared spectroscopy indicated that coordination involved the Lewis acid sites on (activated) hematite (Rochester and Topham, 1979 b).

Infrared spectroscopy showed that SO_2 adsorbed on goethite to form sulphito (OSO_2) species and on lepidocrocite to form sulphate and sulphite complexes (Kaneke and Matsumoto, 1989). XPS measurement suggested that H_2S adsorbed on iron oxide to give both S_8 and SH_3 as surface species, whereas only S_8 formed if the surface had been pre-exposed to water vapour (Prasad et al., 1993).

Adsorption of pyridine on goethite and on hematite involved both coordination to the Lewis acid sites and hydrogen bonding to surface OH groups. Trimethylchlorosilane reacted with the surface OH groups on these oxides to form surface trimethyl siloxyl groups and HCl (Rochester and Topham, 1979 c).

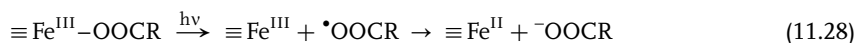
11.8

Photochemical reactions

Iron oxides in the finely divided form have the power to promote (catalyse) a range of redox and photochemical reactions (Tab. 11.7). The preliminary step is the adsorption of the reacting species on the iron oxide. This may be followed either by direct reaction with the Fe surface atoms or surface functional groups or the surface may promote reaction between the adsorbed species and a solution species such as dissolved oxygen.

Iron oxides promote photolysis of various adsorbed species including amino phenols (Pulgarin and Kiwi, 1995), alcohols and amines (Cunningham et al., 1985) and carboxylic acids (Sakata et al., 1984; Cunningham et al., 1988). Irradiation of adsorbed oxalate, benzoate or succinate adsorbed on goethite at pH 5.5–7.5 with UV light ($\lambda = 300\text{--}400 \text{ nm}$) produces $\text{Fe}_{\text{aq}}^{2+}$ and hydroxyl radicals ($\text{OH}^\bullet$) (Cunningham et al., 1988). Various mechanisms for this type of reaction have been suggested. They include direct photolysis, reaction of $\text{OH}^\bullet$ and organic radicals with oxygen leading to formation of H_2O_2 which reacts further with Fe^{2+} and oxygenation of photogenic Fe^{2+} by O_2 .

Photoredox reactions of glycolate adsorbed on goethite produces easily hydrolysed aldehydes (Cunningham et al., 1985), i.e.



The carboxylate free radical rapidly decarboxylates to -hydroxy or -amine radicals which are oxidized by oxygen to formaldehyde or acetaldehyde. Substitution of Mn in the goethite structure reduces the photoredox reactivity of goethite.

Iron oxides promote the oxidation of phenols, a process of importance during the humification of biomass in nature, particularly in soils (Scheffer et al., 1959; Wang et al., 1986). In slightly acid solutions in the presence of finely divided goethite, hydroquinone molecules are converted to quinone (Shido and Huang, 1984). Consumption of O_2 in solution is promoted suggesting that the iron oxide had a catalytic

Tab. 11.7 Reactions catalyzed by iron oxide surfaces.

<i>Oxide</i>	<i>Reaction</i>	<i>Reference</i>
Goethite	Aqueous photolysis of adsorbed ethylene glycol	Cunningham et al., 1985
	Oxidation of catechol and hydroquinone	McBride, 1987
	Aqueous photolysis of benzoate, oxalate and succinate	Cunningham et al., 1988
Lepidocrocite	Reduction of nitrite in the presence of Fe^{2+} ions	Sørensen and Thorling, 1991
FeOOH	Photoreduction of dinitrogen to NH_3	Tennakone et al., 1991
Ferrihydrite	Conversion cyanamide to urea or dicyanamide	Amberg and Vilsmeier, 1978
Hematite	Oxidation of butane to butadiene	Yang and Kung, 1982
	Oxidation of phenolic acids	Lehman et al., 1987
	Dehydrogenation of 1-butene	Liaw et al., 1989
	Oxidation of H_2S	Nowak and Zadrazil, 1991
	Degradation of aminophenols	Pulgarin and Kiwi, 1995
Fe_2O_3	Photoreduction of N_2 to NH_3	Khader et al., 1987

effect on the reaction. It is suggested that a surface Fe^{III} -hydroquinone complex forms which is oxidized to quinone and released into solution together with protons. Catechol is also oxidized, but to a lesser extent, presumably because it is more strongly bound to the goethite surface. Lepidocrocite catalyses Fe^{II} dependent reduction of nitrite to N_2O (chemodenitrification) (Sørensen and Thorling, 1991). The rate of reaction increases as the pH rises from 6 to 8.5. The first step in the reaction is the adsorption of Fe^{II} on lepidocrocite which converts the surface to magnetite.

Photoenhanced adsorption of SO_2 occurs on goethite (Inoue et al., 1988) and on hematite (Toledano et al., 1998). Ultrafine particles of goethite promote photoreduction of adsorbed dinitrogen to ammonia (Tennakone et al., 1991).

Leland and Bard (1987) found that the different iron oxides induced photooxidation of oxalate and sulphite at rates that varied by up to two orders of magnitude. For oxalate, the rate was greater for maghemite than for hematite, but this order was reversed for sulphite. Lepidocrocite (layer structure) induced faster oxidation of both compounds than did the other polymorphs of FeOOH (tunnel structures): the authors considered that the rate differences were probably associated with structural differences between the adsorbents.

Thermal adsorption of NO on hematite took place after the surface atoms of the oxide were reduced to the divalent state by treatment with CO (Rethwisch and Dumescic, 1986). Photoadsorption of NO which was several orders of magnitude greater than that due to thermal adsorption could be induced by treating powdered hematite with aqueous NH_4Cl followed by calcination at ca. 300°C (Blomiley and Seebauer, 1999, 1999a). The reaction appears to be a complex one with water, Cl_2 and Fe^{II} and Fe^{III} being involved.

12

Dissolution

12.1

Introduction

Iron oxides are, in general, compounds with low to very low solubility. In natural systems where most of the iron is in the form of Fe^{III} oxides, the iron should, therefore, be in an immobile form. As large amounts of iron circulate in all parts of the ecosystem (biota, water and soil), however, mobilization of iron (i.e. dissolution) from the oxide reserves must take place.

Examples of mobilization in natural environments include the complexation of Fe by compounds exuded by plant roots, fungi and bacteria, the so-called siderophores (σιδηρόσ, Greek = iron; φέρειν, Greek = carry) and the reduction of ferritin in biota (see Chap. 17). Global Fe mobilization/-immobilization processes are crucial for the formation of iron ores (see Chap. 15) and ferricretes in soils (see Chap. 16) and for the cycling of iron in natural waters. Dissolution processes are also relevant to the interconversions between iron oxides in those cases where the transformation proceeds via solution, especially at low temperatures (see Chap. 13 & 14). The rate at which the precursor dissolves can have a pronounced effect on the type and properties of the final phase.

In industry, processes related to dissolution of iron oxides include acid leaching of iron ores, removal of corrosion products from industrial equipment and heat transfer surfaces (e.g. the cooling coils in water-cooled nuclear reactors), the stability of passive layers on iron, pickling of steel and solar energy conversion/storage by suspensions of iron oxides. In metallurgy, where iron ores are “leached” to recover the metal, the efficiency of the extraction process depends upon the leachability of the ore (Warren & Roach, 1971; Veglio et al., 1994). Removal of iron oxide deposits from the inner surfaces of boilers, steam generators and pipes improves heat transfer, reduces pitting corrosion and prolongs the service life of the equipment. Such corrosion products and also millscale from steel are usually removed using strong acids or acid/complexant mixtures. Sodium dithionite is used to bleach kaolin, i.e. remove the staining iron oxides and thereby improve its whiteness for use in porcelaine (Jepson, 1988).

The dissolution behaviour of iron oxides is usually approached in one of two ways. Corrosion chemists and metallurgists place the emphasis on the electrochemical as-

pects, in particular the effect of the applied potential. This aspect of the dissolution of iron oxides has been treated in reviews by Engell (1956), Vermilyea (1966), Diggle (1973), Segal and Sellers (1984), Frenier and Growcock (1984) and Chiarizia and Horwitz (1991). The other approach, which is emphasized in this chapter, considers the effect of both solution parameters and such properties of the solid as surface area and crystal morphology, on rate. It is aimed at elucidating the principal dissolution mechanisms involved and on the basis of this, developing deterministic, dissolution models.

12.2

Dissolution reactions and mechanisms

12.2.1

General

The principles of dissolution have been reviewed by Bloom and Nater (1991), Blesa et al. (1994) and Casey (1995). The driving force for dissolution is the extent of undersaturation with respect to the oxide. Undersaturation is thus a necessity for dissolution as is supersaturation for precipitation. Other factors being equal, the rate of reaction will increase as degree of undersaturation rises. The extent of undersaturation varies from one system to the next. Dissolution of anodic Fe oxide films often takes place in nearly saturated solutions, whereas extraction of iron from its ores requires markedly undersaturated solutions in order to be efficient. In most natural systems (soils and waters) the aqueous phase is fairly close to saturation with respect to the iron oxides and dissolution may, therefore, be extremely slow. The dissolution process can be accelerated by the presence of higher levels of electrons or chelating ligands.

Most of the data in this chapter was obtained from laboratory experiments in which the dissolution kinetics were followed by monitoring the change in the level of iron released into solution. The dissolution rate and mechanism are often established on the basis of data corresponding to the first few percent of the reaction. (e.g. Stumm et al., 1985). To insure that the initial stages are in fact representative of the behaviour of the bulk oxide (and not an impurity, for example), a complete dissolution curve should be obtained in any investigation.

The factors which influence the rate of dissolution of iron oxides are the *properties of the overall system* (e.g. temperature, UV light), the *composition of the solution phase* (e.g. pH, redox potential, concentration of acids, reductants and complexing agents) and the *properties of the oxide* (e.g. specific surface area, stoichiometry, crystal chemistry, crystal habit and presence of defects or guest ions). Models which take all of these factors into account are not available. In general, only the specific surface area, the composition of the solution and in some cases the tendency of ions in solution to form surface complexes are considered.

Most dissolution studies concentrate on establishing the mechanism of dissolution. There are few studies in which different oxides have been compared to provide

information about the effect of oxide properties. In fact, Blesa and Maroto (1986) conclude that, “there is no unique reactivity which can be attributed to a given oxide”. If this is the case, what differences there are between oxides and even between different samples of the same oxide (after normalizing with respect to surface area), can probably be associated with structural factors. For example, during dissolution, each crystal face should, because it has its own growth rate (at least in aqueous systems), have its own dissolution rate. This, in turn, should lead to what is called shape-preserving dissolution, i.e. the reacting interface should move inwards at a constant rate. This is rarely the case. Real crystal surfaces are seldom smooth on a microscopic scale (see Chap. 4 & 5) and these microheterogeneities lead to surface sites with a range of energies. Such irregularities may be point defects, dislocations, microfractures, kinks, domain boundaries, corners, ledges and edges. Different samples of the same iron oxide may, depending on the formation conditions, contain different types and levels of these irregularities and hence display differences in dissolution behaviour.

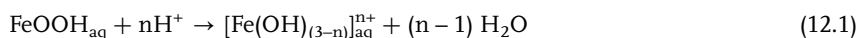
Additives to the solution in which dissolution takes place are of great importance. They may accelerate or retard the process. Additives may act in solution (via complexation), but more often adsorb on the oxide and either raise or lower the energy of attachment between the surface ions and those of the interior. In extreme cases, adsorbed additives may inhibit dissolution. pH has a strong influence on the dissolution of iron oxides. At atmospheric pressure, dissolution of well crystalline Fe^{III} oxides requires a pH of <1 even at 70°C . The high affinity of protons with structural O^{2-} assists the release of iron particularly at low pH. It is the release of the cation, rather than the anions which is likely to be rate limiting. pH also influences the electrochemical surface potential and hence redox processes. The surface potential is determined largely by surface charge, which in turn, depends upon pH (see Chap. 10).

Iron oxide dissolution can proceed by a variety of pathways, viz. protonation, complexation and reduction, photochemical and biological.

12.2.2

Protonation

The general reaction between protons and Fe^{III} oxides can be written as



A detailed mechanism for this heterogeneous reaction has been proposed by Stumm and Furrer (1987); this model is shown in Figure 12.1. Starting with a surface Fe atom coordinated to a neutral OH/OH₂ pair, the first step involves adsorption of a proton by the surface OH group thus transforming the surface $\equiv\text{FeOH}_2$ entity into a positively charged $\equiv\text{Fe}(\text{OH})_2^+$. Subsequently, two more protons per Fe atom are adsorbed. Proton adsorption weakens the Fe-O bond, probably by polarizing it, and so promotes detachment of Fe from the bulk oxide. Figure 12.1 also shows, schematically, the activation energies (E_a) of the various steps; as the detachment step is rate limiting, it is assigned the highest E_a .

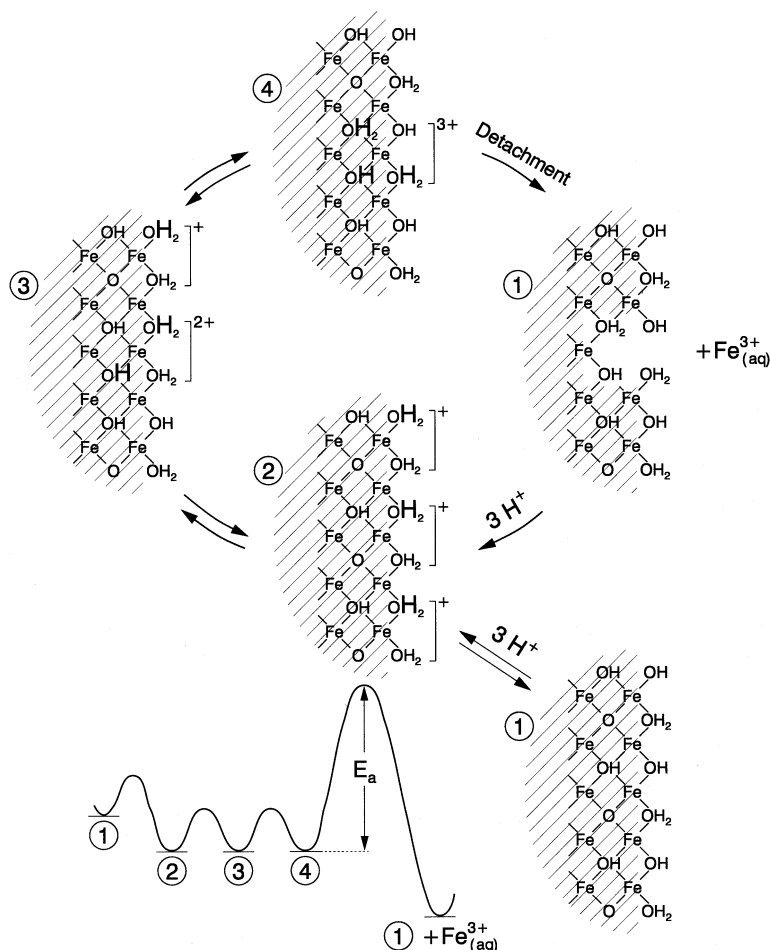


Fig. 12.1 Schematic representation of the consecutive steps of dissolution by protonation of a M^{III} oxide. In the lower part the activation energy, E_a , levels of the corresponding steps are shown (Stumm & Furrer, 1987, with permission).

Initial dissolution of Fe oxides can be very rapid and is then followed by a slower steady state process. The initial step often corresponds to less than 1% of the total solid (Cornell et al. 1974; Maurice et al. 1995). Samson and Eggleston (1998) subjected hematite to a pH jump experiment and found that when the pH was lowered to 1, a reservoir of dissolution active sites on the surface was depleted, but then regenerated when the pH was raised to 2. The authors suggested that these active sites, which made up ~70% of a monolayer, consisted of an “adsorbed nutrient Fe”.

The rate of dissolution by protonation can usually be described by the relationship, $R = k[H_{aq}^+]^n$, with n ranging between 0 and 1 and k being a constant. This arises from the similar relationship between $[H^+]_{aq}$ and adsorbed protons. Classical adsorp-

tion models, such as the Langmuir model, also describe R as a function of adsorbate concentration, $[H^+]_{\text{ads}}$. Although n is often close to 0.5, a linear relationship between R and $[H^+]_{\text{aq}}$ ($n = 1$) has been found for the initial 2–3 % of goethite dissolution (Cornell et al., 1976).

The same principle may hold for the anion accompanying the proton, when the anion replaces surface OH groups and thereby assists in the release of Fe. Cl^- ions have a strong dissolution promoting effect, whereas ClO_4^- , which has a much lower affinity with the oxide surface, does not; sulphate is intermediate. These anions have a similar effect on the dissolution of both natural and synthetic goethite (Surana & Warren, 1969; Cornell et al., 1976).

The rate of dissolution of goethite in HCl is described by the following equation (Cornell et al., 1976),

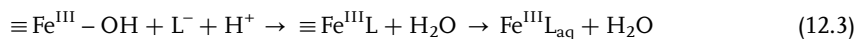
$$\frac{d\text{Fe}}{dt} = k[H^+] \frac{K[N][\text{Cl}^-]}{(1 + K[\text{Cl}^-])} \quad (12.2)$$

where k = reaction rate constant, K = adsorption constant for Cl^- and $[N]$ = number of sites. The concentration of the surface-Cl complex is described by a Langmuir equation which accounts for the fact that the rate is insensitive to solution chloride concentrations above which the surface is fully saturated with adsorbed chloride ions. The effect of chloride was explained as follows; its adsorption lowers the positive surface charge and thus facilitates protonation and in addition, the surface Fe-Cl complex causes weakening of the bond between Fe and neighbouring ions in the bulk oxide. The activation energy for goethite dissolution in HCl and in HClO_4 obtained from runs at 10; 20; 40 and 60 °C was 96 kJ mol⁻¹. It was suggested that dissolution was faster in HCl because the observed E_a also contained a contribution from the adsorption energy of Cl^- and hence, was, in fact, significantly lower than that for HClO_4 .

12.2.3

Complexation

As already shown for chloride ions, complexes of both organic and inorganic ligands with the surface functional groups can substantially increase the rate of dissolution of iron oxides. These ligands may accelerate (ligand promoted dissolution), retard, or even block dissolution. These complexing agents may promote dissolution by either adsorption or by complexation with Fe in solution (Salfity et al. 2000). The first mechanism involves ligand adsorption on the surface of the Fe oxide. This weakens the Fe-O bonds to neighbouring atoms and leads to detachment of the Fe^{III} complex. The general reaction for ligand promoted dissolution may be written as follows:



Examples include the oxalate (10^{-3} M) promoted dissolution of goethite, hematite and ferrihydrite over the pH range 3–5 (Fig. 12.2): in the absence of the ligand, dissolution at this pH is essentially zero (Stumm et al., 1985).

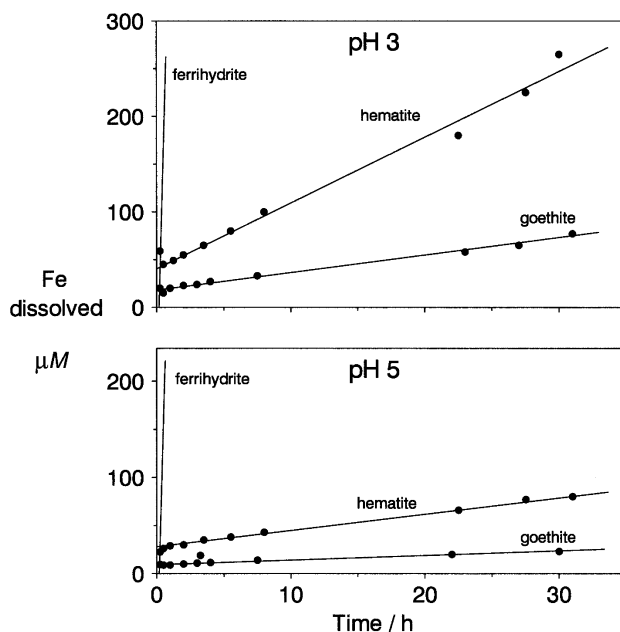


Fig. 12.2 Initial stage of dissolution of ferrihydrite, goethite and hematite in the presence of 10^{-3} M oxalate at pH 3 and 5 (Stumm et al., 1985, with permission).

Stumm and Furrer (1987) proposed that dissolution of an M^{III} oxide by an organic ligand through a surface reaction involved three consecutive reactions, namely, ligand adsorption, metal detachment and proton adsorption/surface restoration as shown in Figure 12.3. Protons facilitate the dissolution process by protonating the OH groups, thereby contributing to a weakening of the Fe-O bond, and, to a lesser extent, act by increasing the positive charge of the oxide surface thus promoting ligand adsorption. On the other hand, as the pH falls, protonation of the ligands in solution increases, the extent of both ligand adsorption and complex formation in solution falls, and thus, the rate of dissolution (by complexation) decreases. As a result of these two opposing processes, i.e. surface protonation and change of ligand speciation, there is often a pH at which the dissolution rate in the presence of an organic ligand is at a maximum. For example, dissolution of hematite in citric acid is at a maximum at pH 4–5, whereas in oxalic acid, the rate continues to increase even at pH 1.5 (Fig. 12.4). Although citrate forms a more stable complex with Fe^{III} , oxalic acid appears to be a more efficient dissolving agent, presumably because adsorption at a particular pH is greater and also because detachment of the Fe-oxalate complex requires breakage of fewer bonds (Zhang et al., 1985). Oxalate adsorption on goethite is constant over the pH range 2–4 and the HOx^- species predominates in solution at pH 2; the dissolution rate is at a maximum at pH 2.6 (Cornell & Schindler, 1987).

Ligands which promote dissolution are thought to form mononuclear (often bidentate) surface complexes, whereas those that inhibit the process form binuclear

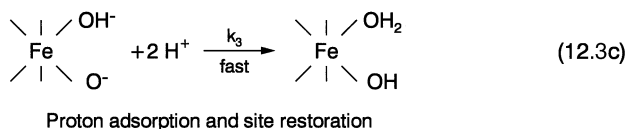
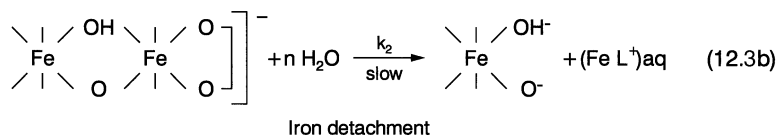
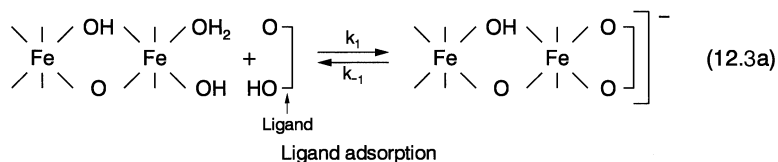


Fig. 12.3 The three subsequent reaction steps of the dissolution of an Fe^{III} oxide by an organic ligand: ligand adsorption, iron detachment and proton adsorption (site restoration) (Stumm & Furrer, 1987, with permission).

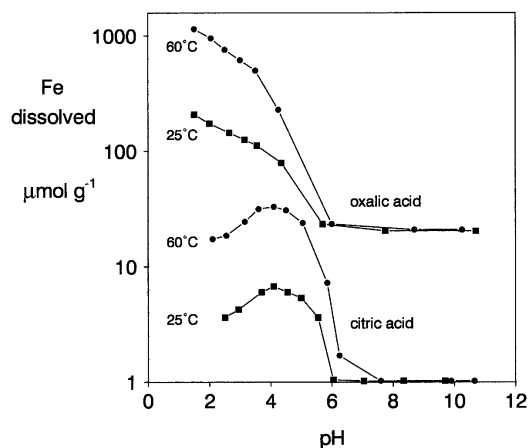


Fig. 12.4 Iron dissolved from hematite in oxalic and citric acid at 25 °C and 60 °C as a function of pH (Zhang et al., 1985, with permission).

(or even trinuclear) surface complexes. The former assist detachment of Fe from the surface, whereas the latter are firmly anchored. The rate of dissolution of goethite by oxalate was retarded by adsorbed chromate and arsenate which formed bidentate surface complexes and thus competed with the adsorbed oxalate species; monodentate surface complexes, however, accelerated dissolution. The effect on rate increased as the surface coverage by chromate and arsenate rose and fell as the pH rose from 3

to 5. At pH 6 the competing ions no longer suppressed dissolution, probably because the surface was now negatively charged ($[-\text{Fe}-\text{O}-\text{CrO}_4]^-$) so that protons could be adsorbed and induce dissolution (Eick et al 1999).

Dissolution of Fe oxides by EDTA is extremely slow in slightly acid media, but for goethite increases to a maximum as the pH is raised to around pH 8. Chang & Matijevic (1982) proposed that as the pH varied, the mechanism by which hematite dissolved in EDTA changed from adsorption mediated at lower pH to a process involving complexation of Fe in solution, in slightly alkaline media. For goethite, on the other hand, the same behaviour was attributed to the formation of a binuclear surface complex at low pH and a mononuclear complex at higher pH (Nowack & Sigg, 1996).

Dissolution of goethite and ferrihydrite at pH 6 by M-EDTA ($M = \text{Pb}, \text{Zn}, \text{Cu}, \text{Co}, \text{Ni}$) is slower than that by EDTA alone (Nowack & Sigg, 1997). Dissolution was considered to involve the formation of a ternary surface complex which then dissociated releasing M into solution after which Fe^{III} was detached from the oxide as Fe-EDTA. For ferrihydrite, the rate of dissolution depended on the nature of M, because the rate determining step was dissociation of M-EDTA. For goethite, on the other hand, this step was fast, hence the rate of dissolution was independent of M.

Mobilization of Fe from Fe^{III} oxides by siderophores is of great importance in natural systems (Emery, 1978; Marschner et al., 1986). The active components of siderophores have been identified as phenolates and hydroxamates. They form very stable Fe^{III} complexes (pK up to 32) and so can mobilize Fe from Fe^{III} compounds (Watanabe & Matsumoto, 1994). This is a widespread mechanism by which biota satisfy their iron needs under conditions where the concentration of mobile Fe in their growth environment is extremely low as, for example, in aerobic, calcareous soils. An example of the extent of mobilization of Fe from goethite by two siderophore producing fungi is documented in Table 12.1 (Watteau & Berthelin, 1990, 1994). Considerable amounts of Fe were solubilized and taken up by the fungi as they developed in a culture medium at pH 3.2–3.8. A separate experiment showed that the oxalic, citric and malic acids excreted by the fungi were not responsible for the goethite dissolution; the active siderophore, however, was not identified. Siderophores have also been suggested as the source of Fe-supply and delivery during synthesis of magnetite in magnetotactic bacteria (Fukomori, 2000).

Tab. 12.1 Amount of iron solubilized from goethite by the two fungi *Suillus granulatus* and *Ustilago sphaerogena* (Watteau & Berthelin, 1990; with permission)

Fungus	6/7	Time/d [§]		
		12/14	18/21	22/32
		Fe/ $\mu\text{g g}^{-1}$ dry biomass		
<i>Suillus</i>	53	27	33	24
ditto + goethite	95	91	184	534
<i>Ustilago</i>	128	33	31	78
ditto + goethite	321	891	988	1260

§ first figure for *Suillus*, second figure for *Ustilago*

Tab. 12.2 Rate equations applicable to dissolution reactions (adapted from Brown et al., 1980 and Giovanoli & Brüttsch, 1975).

Equation	Type	Physical meaning
$\alpha^2 = kt$	Deceleratory	One dimensional diffusion parabolic
$(1 - \alpha) \ln (1 - \alpha) + \alpha = kt$	"	Two dimensional diffusion for a cylinder
$[1 - (1 - \alpha^{1/3})]^2 = kt$	"	Three dimensional diffusion for a sphere
$(1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3} = kt$	"	" " (Ginstling-Brounstein)
$-\ln (1 - \alpha) = kt$	"	Random nucleation (first order)
$[-\ln (1 - \alpha)]^{1/2} = kt$	Variable	Random nucleation (Avrami-Erofejev)
$[-\ln (1 - \alpha)]^{1/3} = kt$	"	" "
$\ln \ln (1 - \alpha) = a \ln k + a \ln t$	"	Modified first order (Kabai)
$1 - (1 - \alpha)^{1/2} = kt$	Geometric	Phase boundary controlled for a shrinking disc
$1 - (1 - \alpha)^{1/3} = kt$	"	Phase boundary controlled for a contracting sphere
$\alpha^{1/n} = kt$	Acceleratory	
$\ln \alpha = kt$	"	

$$J/m_0 = k (m/m_0)^\gamma$$

α = extent of reaction; a = constant; m , m_0 = initial mass of oxide & mass dissolved, resp.

The rate of dissolution of goethite by desferrioxamine B, a fungal siderophore, and desferrioxamine D1, an acetyl derivative of the former, both at a concentration of 240 μM , was found to be 0.02 and 0.17 $\mu\text{mol Fe/hr}$, respectively. Adsorption of these siderophores appeared to be the first step in the process; maximum Fe release at pH 6.6 amounted to 1.5 and 3.5 $\mu\text{mol/g}$ goethite for the two siderophores. (Kraemer et al. 2000). A comparison of three siderophores, viz. mugineic acid (MG), desferrioxamine-B (DFOB) and rhizoferrin (Rh) with the common Fe complexants EDTA and EDDHA showed that the order of Fe^{III} solubilization from 2-line ferrihydrite after 15 d at pH 8.7 was control ~ EDTA < Rh ~ MA < EDDHA > DFOB (Shenker et al. 1999). At concentrations above 200 μM , oxalate enhanced the rate of dissolution of Al-goethite by desferrioxamine B (Cervini-Silva & Sposito, 2002). A soil bacterium siderophore (0.24 mM) dissolved hematite ($\text{SA} = 29\text{m}^2/\text{g}$) at 21 °C and pH 3 at a rate of $10^{-8} \text{ mol m}^{-2} \text{ h}^{-1}$, i.e. 5 times more slowly than did oxalate or ascorbate of similar concentrations (Hersman et al. 1995). Phosphate, because of its high affinity with the Fe oxide surface, inhibited Fe dissolution by mugineic acid mainly by displacement of the acid from the surface of Fe oxides (Hiradate & Inoue 1998).

In soils and other geoenvironments, water soluble humic compounds are also candidates for complexation and release of Fe from Fe oxides and thereby may provide Fe for plants. For example, compared to the control, water extractable humics from peat (1.7 mmol C/L) doubled the amount of Fe extracted from a freshly prepared 2-line ferrihydrite over 24 hr (Cesco et al. 2000).

12.2.4

Reduction12.2.4.1 **General**

A third mechanism by which the structural bonds between Fe atoms in iron oxides may be weakened involves reduction of structural Fe^{III} to Fe^{II} . In natural environments, reductive dissolution is by far the most important dissolution mechanism. It is mediated both biotically and abiotically. The most important electron donors, particularly in near surface ecosystems result from metabolic oxidation of organic compounds under O_2 deficient conditions. In anaerobic systems, therefore, the availability of Fe oxides i.e. the electron sink, may control the degradation of dead biomass and organic pollutants in the ground water zone (see chap. 21). Reductive dissolution is also often applied to the removal of corrosion products from piping in industrial equipment and the bleaching of kaolin.

In view of its importance, reductive dissolution of Fe oxides has been widely studied. Reductants investigated include dithionite, thioglycolic acid, thiocyanate, hydrazine, ascorbic acid, hydroquinone, H_2S , H_2 , Fe^{2+} , tris (picolinato) V^{II} , fulvic acid, fructose, sucrose and biomass/bacteria (Tab. 12.3). Under the appropriate conditions, reductive dissolution may also be effected photochemically. As with protonation, the extent of reduction may be strongly influenced by ligand and proton adsorption on the oxide surface.

Reductive dissolution may be more complex than the two previous mechanisms in that it involves electron transfer processes. Formation of Fe^{II} via reductive dissolution can be effected by adsorption of an electron donor, cathodic polarization of an electrode supporting the iron oxide and by transfer of an electron from within a ternary surface complex to a surface Fe^{III} . Addition of Fe^{II} to a system containing a ligand such as EDTA or oxalate promotes electron transfer via a surface complex and markedly accelerates dissolution.

As in the case of protonation, the detachment of Fe is likely to be rate determining, but it cannot be ruled out that, as has been suggested for Mn oxides, electron transfer is, in some cases, rate limiting (Stone & Morgan, 1987). Reduction of Fe^{III} to Fe^{II} destabilizes the coordination sphere of the iron both as a result of the loss of charge and because of the larger size of the bivalent Fe^{II} (0.078 nm vs. 0.064 nm) and thus induces detachment of iron as Fe^{2+} from the structure. It is often difficult to determine experimentally the step which involves formation of Fe^{II} . On the basis of a kinetic study of the dissolution of magnetite by reducing mercapto carboxylic acids, Borghi et al. (1991) concluded that the distinction between the reduction of structural Fe^{III} in a surface $\text{Fe}^{\text{III}}\text{L}$ complex followed by Fe^{II} detachment and the formation of a soluble $\text{Fe}^{\text{III}}\text{L}$ complex followed by its reduction in solution is often ambiguous and that the two processes are kinetically equivalent.

Detachment of structural Fe is again facilitated by protonation of the metal site. Because the reducing ligand is (usually) a charged species, pH will, through its effect on extent of ligand adsorption, have a strong effect on the rate of reductive dissolution. This will be a function of both pH and the concentration of ligand in solution. Borghi et al. (1991) consider that the strong pH dependence of the rate of reductive

Tab. 12.3 Dissolution experiments with single samples of different iron oxides.

Oxide*	Dissolving medium	Concentration/M Wave length/nm	T/°C	pH	Kinetic model	Type of dissoln.**	Reference
Gt	HCl	0.5	10–60	–	cube root	P	Cornell et al., 1974
Gt	oxalate light	0.025 UV	25	2.6	–	R, C	Cornell & Schindler, 1987
Gt	Na ₂ S ₂ O ₄ citrate EDTA	1–20 · 10 ⁻³ 0–0.2 0–0.1	30–80	4–9	–	R, C	Rueda et al., 1992
Gt	EDTA	0–8 · 10 ⁻³	30, 50	2–12	–	C	Rueda et al., 1985
Gt	13 org. acids including lactic, citric, tartaric	2.5 · 10 ⁻³	23	3.5; 5.5	–	P, C	Miller et al., 1986
Gt	HCl, HNO ₃ , H ₂ SO ₄ carboxylic acids diphosphonic acids Na ₂ S ₂ O ₄ , ascorbic acid formaldehyde desulfoxylate	0.5–12	25–80	–	1st order rate cubic root	P, R	Chiarizia & Horwitz, 1991
Gt	HCl	6	25	–	Kabai	P	Schwertmann et al., 1985
Gt (Al, Mn, Cr, V)	HCl	6	25	–	Kabai; Avrami-Erovezhev	P	Schwertmann, 1984a, 1991, unpubl.
Gt nat.	HCl	2	25	–	Kabai	P	Schwertmann et al., 1987
Lp	citrate light	n.g. [§] > 295	n.g.	n.g.	–	R, C	Waite & Morel, 1984

* Gt: goethite; Lp: lepidocrocite; Ak: akaganéite; Fh: ferrihydrite; Hm: hematite; Mt: magnetite; Mh: maghemite; Wü: wüstite

** P: protonation; R: reduction; C: complexation; § n.g.: not given

Tab. 12.3 (continued)

Oxide*	Dissolving medium	Concentration/M Wave length/nm	T/°C	pH	Kinetic model	Type of dissoln. ***	Reference
Lp	HCl	1	76	–	cube root	P	Cornell & Giovanoli, 1988 a
Ak	EDTA	$0-6 \cdot 10^{-3}$	22–90	2–12	–	C	Rubio & Matijevic, 1979
Ak	HCl	1	76	–	Avrami-Erofejev	P	Cornell & Giovanoli, 1988 a
Fh	Polyposphate	$5 \cdot 10^{-4} - 10^{-2}$	1.5, 25	5	–	P, C	Lin & Benjamin, 1990
Hm	X-rays	–	n.g.	2.2	–	R, C	Buxton et al., 1982
	propanol-2-ol	0.1					
	EDTA	$1 \cdot 10^{-3}$					
Hm	bisulfate	$2 \cdot 10^{-4}$	25	ca. 3	–	R	Faust & Hoffmann, 1986
	light	350–676					
Hm	aminocarboxylic acids (EDTA etc.)	$10^{-3} - 10^{-1}$	26–120	3.3–10	–	C	Chang & Matijevic, 1983
Hm	Na_2SO_3	$2 \cdot 10^{-4}$	25	2.86–2.96	–	P, R	Faust & Hoffmann, 1986
	light	350–676					
Hm	oxalate		20	3	–	P, R, C	Siffert & Sulzberger, 1991
	light	350–405					
Hm	KSCN	1.47–1.72	80	2.0–2.8	–	R, C	Regazzoni & Blesa, 1991
Hm	tris (picolinato) V^{II}	$2 \cdot 10^{-3}$	RT	n.g.	cube root	R, C	Segal & Sellers, 1982
Hm	α -mercapto carboxylic acids	$1-20 \cdot 10^{-3}$ > 423	10–35	3; 4	cube root	R	Waite et al., 1986
Mt	EDTA	0.1	25	4–8	–	R, C	Blesa et al., 1984
	Fe^{2+}	0.1–0.2					

* Gt: goethite; Lp: lepidocrocite; Ak: akaganéite; Fh: ferrihydrite; Hm: hematite; Mt: magnetite; Mh: maghemite; Wü: wüstite

*** P: protonation; R: reduction; C: complexation; § n.g.: not given

Tab. 12.3 (continued)

Oxide*	Dissolving medium	Concentration/M Wave length/nm	T/°C	pH	Kinetic model	Type of dissoln.**	Reference
Mt	thioglycolic acid	0.03–0.72	30–50	2–7	–	R, C	Baumgartner et al., 1982
Mt	EDTA Fe ²⁺	0.1 1–2 · 10 ⁻³	30	3–8	–	R, C	Blesa et al., 1984
Mt	nitrilo-triacetato ferrat Fe ²⁺	0–0.3 0–0.4	n.g.	3–5	–	R, C	Del Valle Hidalgo et al., 1988
Mt	H ₂ SO ₄ Fe ²⁺	0–0.2	70–90	–	cube root	R, P	Bruyere & Blesa, 1985
Mt	mercapto-carboxylic acids Fe ²⁺	0.033–0.6 1.3 · 10 ⁻³	55 RT	2.5–5.5	–	R, C	Borghiet al., 1991
Mt	oxalate Fe ²⁺	0.1–0.3 0–2.3 · 10 ⁻³	30	3–9	–	C, R	Blesa et al., 1987
Mt	ascorbic acid	1–7 · 10 ⁻²	51.8–81.2	2.54–3.40	–	C, R	Dos Santos Afonso et al., 1990
Mt	EDTA Fe ²⁺	0–2 · 10 ⁻² 0–10 ⁻¹	25	3.0–4.5	–	C, R	Borghiet al., 1989
Co-Mt	thioglycolic acid Fe ²⁺	0–0.65 0–0.9 · 10 ⁻³	70	–	cube root	R, C	Blesa et al., 1986
Mh	oxalate EDTA Fe ²⁺ light	0.016 0.02–0.04 3 · 10 ⁻⁴ 254	n.g.	3; 4	–	R, C	Litter & Blesa, 1988

* Gt: goethite; Lp: lepidocrocite; Ak: akaganéite; Fh: ferrihydrite; Hm: hematite; Mt: magnetite; Mh: maghemite; Wü: wüstite

** P: protonation; R: reduction; C: complexation; § n.g.: not given

Tab. 12.3 (continued)

Oxide*	Dissolving medium	Concentration/M Wave length/nm	T/°C	pH	Kinetic model	Type of dissoln. **	Reference
Mh	KSCN light	$5 \cdot 10^{-2}$; 2 254, 366, 450	20, 30	2; 7	–	C, P, R	Litter & Blesa, 1990
Gt, Hm	HCl HClO ₄ H ₂ SO ₄ SO ₂	0.15–2.0 15.8–158 kPa	70–120	–	–	P R	Surana & Warren, 1969 Warren & Roach, 1971
Gt, Hm	HCl	1	40–70	–	cube root	P	Lim-Nunez & Gilkes, 1987
Gt, Hm	Na dithionite citrate	0.25	25	8	–	R, C	Torrent et al., 1987
Gt, Hm	Fe ²⁺ oxalate malonate ascorbate Al	$0-120 \cdot 10^{-6}$ $0.5-1 \cdot 10^{-3}$	25 25	2–4	–	R, C	Suter et al., 1991 Banwart et al., 1989
Gt, Hm	phenols	$1 \cdot 10^{-3}$	30	2–6	–	R	LaKind & Stone, 1989
Gt, Hm	HCl	1; 0.1	6.5	–	Avrami-Erofejev	P	Cornell & Giovanoli, 1993
Hm, Mt	EDTA hydrazine	0.1 10 g L ⁻¹	92	4–10	–	C, R	Torres et al., 1990
Hm, Mt	ascorbic acid dehydroascorbic acid oxalate EDTA	$0.7 \cdot 10^{-2}$ $5 \cdot 10^{-5}$ $0-2 \cdot 10^{-2}$	25, 65	2–5	–	C, R	Dos Santos Afonso et al., 1990a

* Gt: goethite; Lp: lepidocrocite; Ak: akaganéite; Fh: ferrihydrite; Hm: hematite; Mt: magnetite; Mh: maghemite; Wü: wüstite

** P: protonation; R: reduction; C: complexation; § n.g.: not given

Tab. 12.3 (continued)

Oxide*	Dissolving medium	Concentration/M Wave length/nm	T/°C	pH	Kinetic model	Type of dissoln.**	Reference
Hm, Mh	EDTA light	$1 \cdot 10^{-2}$ 254, 366, 450		2; 7	–	C, P, R	Litter & Blesa, 1988
Hm, Mh	EDTA oxalate light Fe^{2+}	$1 \cdot 10^{-2}$ 0.016 < 400 $2.65 \cdot 10^{-4}$	30, 70	3–4	–	P, R, C	Litter & Blesa, 1988 Litter et al., 1991
Gt, Fh, Hm	HNO_3 oxalate ascorbic acid	$2.5-10 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	25	1.5–6.0	–	P C R, C	Zinder et al., 1986
Gt, Fh, Hm	13 organic acids fulvic acid		23	3.5; 5.5	–	C	Miller et al., 1986
Hm, Mt, Mh	EDTA Fe^{2+} light	$2 \cdot 10^{-2}$ $5.1-6.1 \cdot 10^{-5}$ 254	30	3	–	C, R, P	Litter & Blesa, 1992
Gt, Lp, Hm, Mt	H_2S	10–1000 Pa	25	3–7	–	R	Dos Santos Afonso & Stumm, 1992
Gt, Lp, Fh, Hm	H_2	Eh: -0.3 to 0.1 V	RT	3	–	R	Fischer, 1987
Gt, Lp, Hm, Mt, Mh	HCl HClO_4	0.1–2.0	10–60	–	–		Sidhu et al., 1981
Hm, Mt, FeO	H_2SO_4 , HCl, H_3PO_4 , Na_2EDTA		80 °C		$-\ln(1-a) =$ Asinhkt	P	Gorichev & Kipryganov, 1984

* Gt: goethite; Lp: lepidocrocite; Ak: akaganéite; Fh: ferrihydrite; Hm: hematite; Mt: magnetite; Mh: maghemite; Wü: wüstite

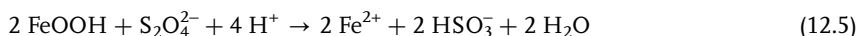
** P: protonation; R: reduction; C: complexation; § n.g.: not given

dissolution of magnetite in mercapto carboxylic acids (maximum at pH 3–4), indicates that moderately strong attachment of the ligand to the surface is optimal for polarization of the Fe-O bond, whereas strong bonding lowers the dissolution rate by immobilizing a surface site.

It is to be expected that reductive dissolution of Fe oxides becomes faster as the electron activity increases, i.e. the lower the redox potential (Eh) of the aqueous system, the faster the dissolution. Fischer (1987) dissolved goethite at pH 3 and RT in an Eh range of between –0.3 and +0.1 V and found that the dissolution rate, $\ln k$, decreased linearly from about 5 to 1 mg Fe²⁺ L^{–1} min^{–1} ($r^2 = 0.96$). Organic and inorganic additives that shift the redox potential in a negative direction, accelerate dissolution of iron oxides (Frenier & Growcock, 1984).

12.2.4.2 Examples of reductants

Sodium dithionite (Na₂S₂O₄) is a reductant that is commonly used for the extraction of Fe oxides from kaolin and from soils (both to determine the total amount of Fe oxides and to improve the dispersibility of the clay minerals; Mehra & Jackson, 1960). The overall reaction may be written as:



This reduction reaction is counterbalanced by disproportionation of dithionite, i.e.



The rate of disproportionation increases with decreasing pH and rising temperature and these conditions also favour oxide reduction. To achieve a reasonable rate of dissolution, one has to compromise on the pH. A pH of 3 is used in kaolin bleaching (Jepson, 1988), whereas in soil analysis the system is usually buffered with citrate and bicarbonate at ca. pH 7 (Mehra & Jackson, 1960). Citrate also complexes the dissolved Fe²⁺ and prevents its precipitation as Fe^{II} sulphide. For the dithionite/EDTA system, Rueda et al. (1992) found a maximum efficiency at pH 5–6 and an activation energy for goethite dissolution of 70 kJ mol^{–1}. They stressed the importance of adsorption of S₂O₄^{2–} on the surface to ensure reduction of Fe^{III}.

Other examples of complexing agents which act together with reducing agents are Cl[–] which promoted reductive dissolution of hematite and magnetite by Cr²⁺ (Bradbury et al., 1983) and aqueous V³⁺ which enhanced the reductive dissolution of wüstite and magnetite (Valverde, 1976). Similar synergistic effects were displayed during the reduction of ferrihydrite and goethite by Fe²⁺ (Fischer, 1972) and of goethite by ascorbic acid (Stumm et al., 1985), both in the presence of oxalate. The initial (ca. 2%) dissolution rate was a direct function of the level of adsorbed oxalate (Fig. 12.5; insert). Because both the complexing ligand (oxalate) and the reductant must be adsorbed before they interact with the oxide, their surface complexation constants strongly influence the dissolution rate (Rueda et al., 1992). Sucrose was found to be an effective reductant for dissolution of hematite in sulphuric acid (Veglio et al., 1994); this process is used for bleaching of kaolin and quartz bearing sands.

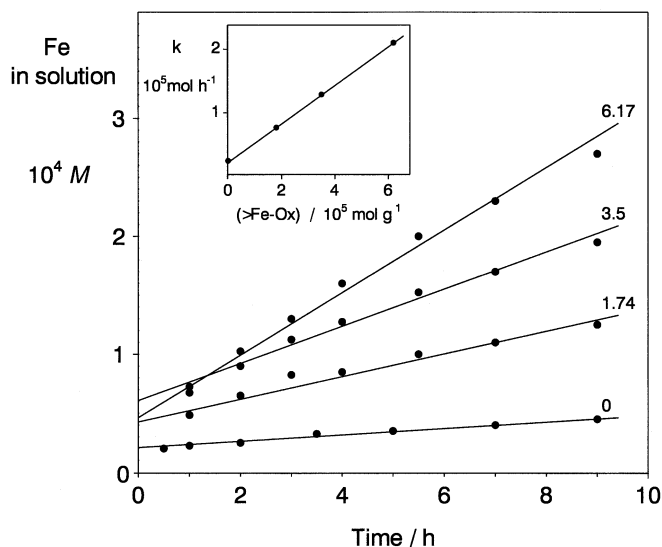


Fig. 12.5 Dissolution-time curves of synthetic goethite in 10^{-3} M ascorbic acid at pH 4 with various amounts of oxalic acid adsorbed by the goethite (figures at the curves). Insert: relationship between the initial dissolution rate k and the amount of oxalate adsorbed by the goethite (Stumm et al., 1985, with permission).

Reducing agents such as thioglycolic acid (Baumgartner et al., 1982), oxalic acid (Baumgartner et al., 1983) and tris (picolinato) V^{II} (Segal & Sellers, 1982) are used, or have the potential to be applied, to decontaminate pipes in water cooled nuclear reactors; hematite and magnetite were studied as model oxides. The first step in the process involves adsorption of the reductant. Thioglycolic acid dissolution of magnetite is at a maximum at pH 4–5; this is the result of a balance at this pH between two opposing parameters – the thioglycolate concentration, which increases with rising pH, and the positive surface charge which rises as pH falls (Baumgartner et al., 1982).

Various phenolic reductants have been used to dissolve synthetic goethite and hematite (LaKind & Stone, 1989). In hydroquinone, goethite dissolved according to the following reaction:



where QH_2 and Q are hydroquinone and quinone, respectively. In hydroquinone and methylhydroquinone, a maximum rate was noted at around pH 3.5–4.0, whereas in pyrogallol, the rate increased consistently as the pH decreased (Fig. 12.6). Both rates paralleled the extent of adsorption of these organics. Reductive dissolution by phenols may be important in the formation of Fe^{2+} in acid surface soils, e.g. during podsolization (see Chap. 16) and in the rhizosphere where phenolic compounds have been identified as products of humification and as root exudates, re-

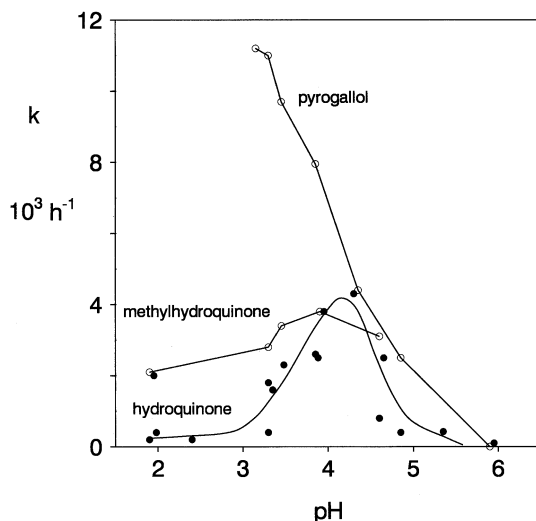


Fig. 12.6 The effect of pH on the dissolution rate of goethite in various phenols (LaKind & Stone, 1989, with permission).

spectively. Bloomfield (1957) demonstrated that a range of extracts from both fresh and decomposing tree leaves, mainly the low molecular weight fraction, had a remarkable ability to dissolve a synthetic Fe oxide (probably ferrihydrite) abiotically even under neutral and aerobic conditions; a combination of reduction and complexation reactions was involved. It was the low molecular weight fraction of the leaf extract which was active, whereas the high molecular weight fraction impeded the dissolution process, most probably by blocking the surface sites on the oxide in a manner similar to that noted for EDTA.

Fe^{2+} ions accelerate the dissolution of Fe oxides (Lieser & Schroeder, 1959). Increasing $[\text{Fe}^{2+}]$ increased the rate of dissolution of ferrihydrite in oxalate at pH 3 (Fig. 12.7) with the initial rate being linearly related to $[\text{Fe}^{2+}]^{0.5}$ (Fischer, 1972). The same effect was observed for goethite (Fig. 12.8, left) with there being a linear relationship between $\log \text{Fe}_{\text{released}}$ and $[\text{Fe}^{2+}]_{\text{aq}}$ (Suter et al., 1991). Although the rate increased initially with rising $[\text{Fe}^{2+}]$, it levelled off at higher concentrations. The rate also increased as the pH rose from 2 to 4 owing to increasing deprotonation of oxalate which facilitates adsorption (Fig. 12.8, right). At even higher pH, adsorption decreased, partly because the oxide surface became less positive, but also because Fe^{2+} may have been deactivated by oxidation. It is generally agreed that in the Fe^{2+} /oxalate system, the first step is formation of a soluble Fe^{II} oxalate complex which adsorbs at a surface Fe^{III} site. The Fe^{II} -oxalate complex is considered to be a much stronger reductant than Fe^{2+} alone. Upon adsorption, an electron is transferred from the $\text{Fe}^{\text{II}}\text{-(ox)}_n^{(2n-1)}$ surface complex to a surface Fe^{III} site thus inducing detachment of Fe and creation of a new surface site.

In addition to oxalate, malonate and citrate accelerate the dissolution of iron oxides in the presence of Fe^{2+} (Sulzberger et al., 1989). Fe^{2+} also promotes the dissolution of magnetite in sulphuric acid (Bruyere & Blesa, 1985). Small amounts of Fe^{2+} in solution speed up the transformation of ferrihydrite to goethite at 50 °C (see Fig. 14.24) by promoting the dissolution of ferrihydrite (Fischer, 1972). Adsorption

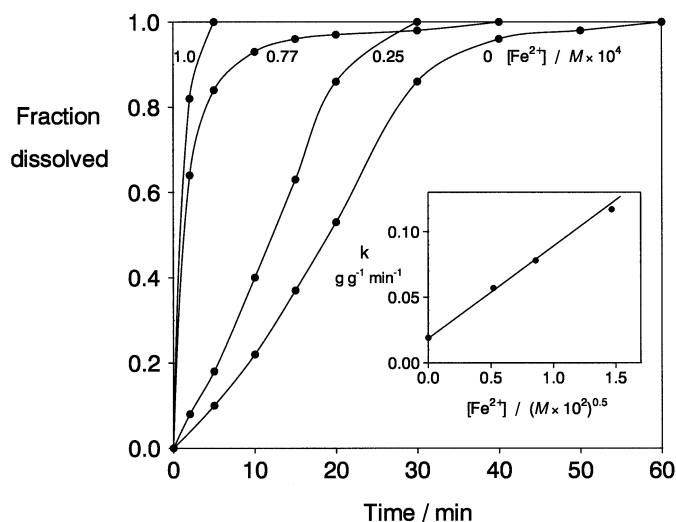


Fig. 12.7 Dissolution-time curves of 2-line ferrihydrite in 0.2 M NH_4 oxalate pH 3.0 in the presence of various $[\text{Fe}^{2+}]$ (0 – $1.3 \cdot 10^{-4} \text{ ML}^{-1}$) at RT. Insert: initial rate of dissolution, k , as a function of $[\text{Fe}^{2+}]^{0.5}$ (Fischer, 1972, with permission).

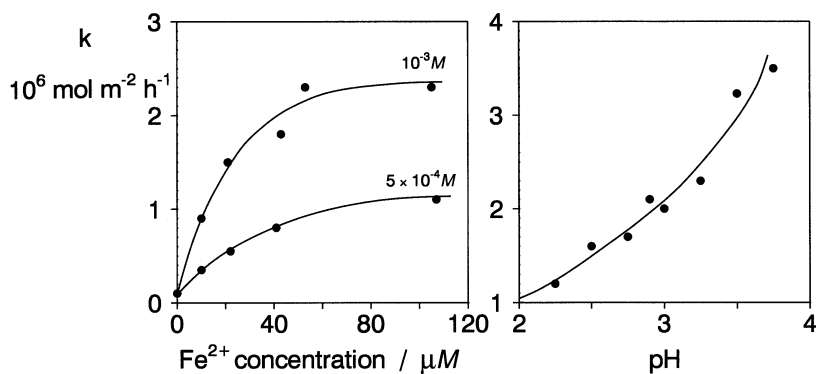


Fig. 12.8 Left: dissolution rate of goethite at 25 °C in 10^{-3} and $5 \cdot 10^{-4} \text{ M}$ oxalate at pH 3.0 as a function of $[\text{Fe}^{2+}]$. Right: same as a function of pH ($[\text{Fe}^{2+}]$: $5 \cdot 10^{-3} \text{ M}$; oxalate: 10^{-3} M) (Suter et al., 1991, with permission).

of Fe^{2+} is a necessary first step in the dissolution process. Only a small amount of Fe^{2+} is required for the reaction to proceed to completion, because upon reoxidation of the detached Fe^{2+} in solution (to form goethite), the electron is again available for further interaction with ferrihydrite. In other words, there is no net reduction and so the dissolution process may be considered to be reductively catalysed.

Dissolution of iron oxides is also promoted by free radicals generated by irradiation of colloidal suspensions. Buxton et al. (1982, 1983) irradiated a monodisperse

suspension of hematite in the presence of 2-propanol and nitrous oxide. The 2-propanol acted as a scavenger and interacted with the intermediates formed by the radiolysis process to form the $(\text{CH}_3)\dot{\text{C}}\text{OH}$ radical, a powerful, one electron reductant which dissolves the solid, i.e.



As the radical tends to disproportionate, the rate of dissolution gradually decreases. Addition of EDTA to the system greatly enhances the dissolution owing to the formation of $\text{Fe}^{\text{II}}\text{-EDTA}$ which dissolves the oxide via a thermal pathway. In the presence of 2-propanol, the $\text{Fe}^{\text{II}}\text{-EDTA}$ is continually regenerated and thus acts as a catalyst. Similar behaviour has been observed for magnetite particles (Segal & Sellers, 1984).

12.2.4.3 Photochemical reduction

Light of the appropriate wavelength may promote reductive dissolution by supplying energy for charge transfer among the surface $\text{Fe}^{\text{III}}\text{OH}$ groups both by inducing photolysis of Fe^{III} -ligand complexes and by creation of electron/hole pairs in semiconductors. Frequently, ligands such as oxalate, citrate and thioglycolate which assist in complexation dissolution can, if photochemically activated, dissolve iron oxides reductively. A practical example of photoreductive dissolution is the formation of Fe^{2+} in surface waters as a result of diurnal fluctuations (McKnight et al., 1988) (Fig. 12.9). Fe^{II} also forms in atmospheric water droplets with levels of up to 10^{-3} M being found in urban fogs (Faust & Hoffmann, 1986). Photoreductive dissolution has been used to determine the total amount of iron oxides in soils and sediments by suspension of the solid in acid oxalate solution under the influence of UV light (Tamm, 1932; De Endredy, 1963; Schwertmann, 1964).

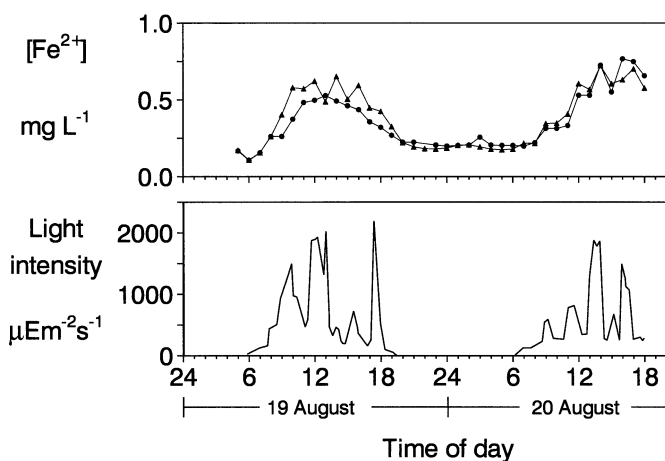


Fig. 12.9 Changes of $[\text{Fe}^{2+}]$ and light intensity vs. time over two days at two locations of St. Kevin Gulch, Colorado, USA (McKnight et al., 1988, with permission).

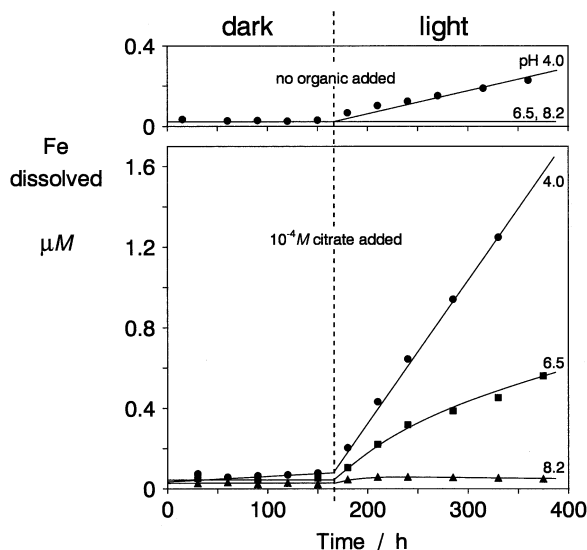
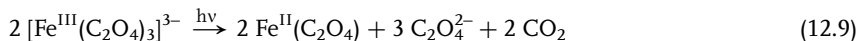


Fig. 12.10 Dissolution-time curves of lepidocrocite ($5 \mu\text{M}$) in dark and light ($300 \mu\text{E cm}^{-2} \text{ min}^{-1}$) conditions at various pH's in the absence (top) and presence (bottom) of 10^{-4} M citrate (Waite & Morel, 1984, with permission).

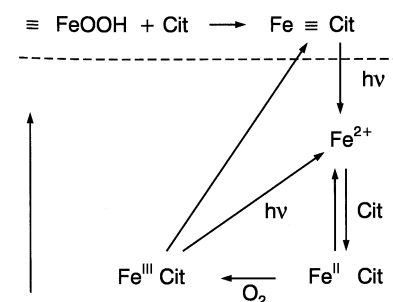
Systematic studies of photochemical dissolution of hematite (Waite, 1986), lepidocrocite (Waite & Morel, 1984) and goethite (Cornell & Schindler, 1987) have been carried out. Figure 12.10 illustrates the combined effect of light, an organic complexing agent and pH on the release of Fe from a synthetic lepidocrocite. Light is the main cause of accelerated dissolution, but as would be expected, the process is also enhanced by the presence of citrate and protons. In addition to its role as a complexing agent, the Fe^{III} -citrate surface complex may facilitate light induced electron transfer (Waite & Morel, 1984). A possible reaction mechanism is shown in Figure 12.11 (left).

Photochemical dissolution of goethite ($88 \text{ m}^2 \text{ g}^{-1}$) in an oxalate buffer solution has been induced by irradiation with unfiltered UV light (Cornell & Schindler, 1987). Release of Fe^{3+} followed a sigmoidal curve with two moles of H^+ being consumed per mole Fe released and equal quantities of CO_2 (from oxalate decomposition) and Fe^{2+} being formed (Fig. 12.12 top). The rate of dissolution at pH 2.6, expressed in terms of H^+ consumption (Fig. 12.12 bottom), was $0.15 \text{ mol H}^+ \text{ min}^{-1} \text{ m}^{-2}$. Dissolution was a maximum at pH 2.6 most probably because at this pH, the combination of falling $[\text{H}^+]$ and rising [oxalate] as the pH rose, was optimized. Addition of 0.9 mmoles Fe^{2+} at the start of the reaction eliminated the induction period, but did not accelerate the subsequent reaction. A possible mechanism for the dissolution process is shown in Figure 12.11 (right). As a first step, oxalate adsorbs to form a Fe^{III} -oxalate surface complex which is slowly released into solution (thermal dissolution) and then photochemically reduced to an Fe^{II} -oxalate complex together with oxalate and CO_2 , i. e.



The Fe^{II} -oxalate complex then adsorbs on goethite (step 2) where it exchanges an electron with a surface Fe^{III} atom to form Fe^{II} (step 3) and is itself reoxidized.

SOLID PHASE



SOLUTION PHASE

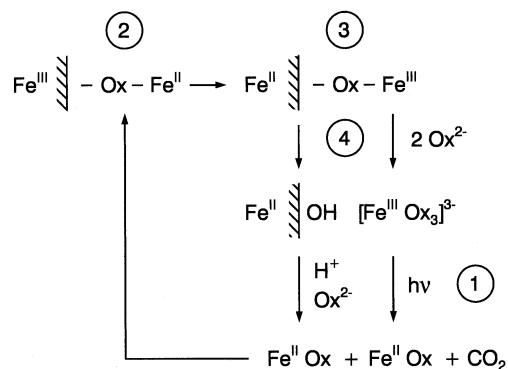


Fig. 12.11 Reaction schemes suggested for the photochemical reduction of lepidocrocite in the presence of citrate (left) (Waite & Morel, 1984, with permission) and of goethite in the presence of oxalate (right) (Cornell & Schindler, 1987, with permission).

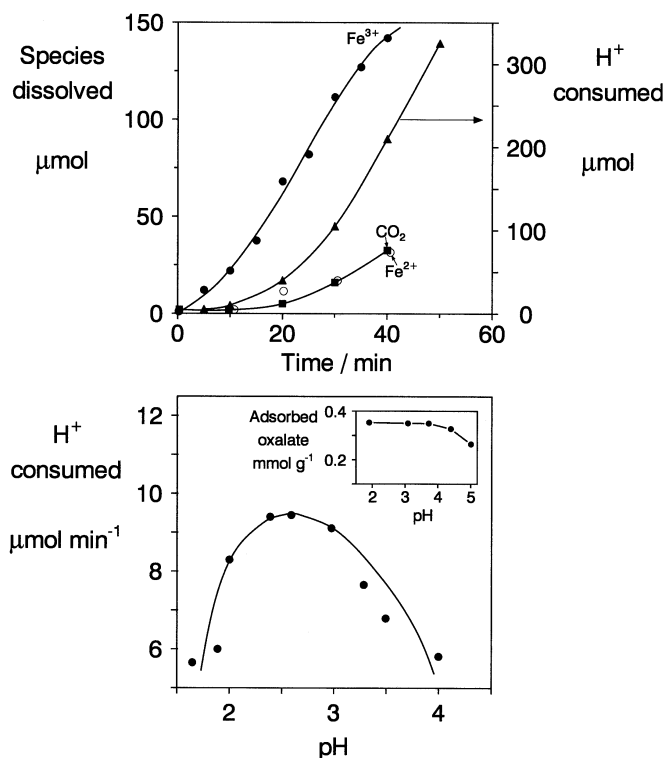


Fig. 12.12 Top: Fe³⁺ and Fe²⁺ release from synthetic goethite, CO₂ production and H⁺ consumption as a function of time in the presence of 0.025 M oxalate at pH 2.6 and 25 °C. Bottom: The effect of pH on the rate of photochemical dissolu-

tion of goethite in 0.2 M H₂C₂O₄/K₂C₂O₄ mixtures under the influence of UV light as measured by the level of H⁺ consumed. Insert: oxalate adsorption by goethite as a function of pH (Cornell & Schindler, 1987, with permission).

Desorption of the reduced metal ion is the rate determining step and is assisted by protons and oxalate ions. The reoxidized surface complex also desorbs owing to its altered molecular structure and is thus available for further reaction. The reductive dissolution step is faster than the initial complexation process. Photochemical dissolution of hematite in acidic oxalate solution is faster when air is excluded from the system (by purging with N_2) than when air is present (Taxiarchou et al. 1997).

The E_a for the dissolution of hematite by mercapto carboxylic acids in acid media in the presence of UV radiation was lower ($64 \pm 5 \text{ kJ mol}^{-1}$) than that for dissolution in the absence of radiation ($94 \pm 8 \text{ kJ mol}^{-1}$) (Waite et al. 1986). The reaction in both cases was considered to involve formation of an intermediate organic-Fe surface complex which decomposed as a result of intramolecular electron transfer to release Fe^{II} . UV irradiation enhanced the decomposition of the surface complex either through excitation of the ligand field states associated with the free electrons on the S atoms, or through high energy charge transfer states.

Litter et al. (1991) found that the dissolution of maghemite was also considerably speeded up, once a dissolved Fe^{III} -oxalate or Fe^{III} -EDTA complex was reduced to an Fe^{II} complex by UV irradiation ($\lambda = 254 \text{ nm}$). This system also showed an induction period which could be eliminated by addition of Fe^{2+} (see Fig. 12.28). In a study concerned with dissolution of corrosion oxide, electrons from viologen radicals produced by γ -radiation (^{60}Co) were used to dissolve hematite and goethite (Mulvaney et al., 1988); it was observed that the Fe^{2+} appearing in solution could only account for a fraction of the electrons consumed. The remainder was involved in conversion of the Fe^{III} oxide into magnetite.

12.2.4.4 Biological and other reduction reactions

There have been numerous laboratory studies of the microbiological reduction of iron oxides by certain bacteria under controlled conditions (see Fischer, 1988 and Lovley, 1992, 1997 for reviews). The principle behind this process is the potential of Fe^{III} in solid Fe oxides to accept electrons from the biogenic dissimilation (oxidation) of organic compounds. This occurs once oxygen is no longer present as an e^- acceptor, i.e. under anoxic conditions. A number of these studies used such strains of the dissimilatory iron reducing bacteria *Shewanella alga*, *Sh. putrefaciens*, *Geobacter metallireducens*, and others with various carbon sources, such as malonate and lactate supplying the necessary energy for reduction and adenosine triphosphate (ATP) as the energy carrier. This process is extremely important in the metabolization and, thus, detoxification of organic pollutants in anthropogenic environments (see chap. 21). The products of oxidation are electrons and metabolites which upon complete oxidation go to CO_2 and H_2O . As described earlier, both the electrons and the protons thus produced are transferred to the oxide surface, thus causing formation and detachment of Fe^{2+} . A bulk reaction equation can be written as,



where CH_2O stands for the biomass.

Liu et al. (2001) summarized the factors determining the rate of biotic Fe^{III} reduction as follows: direct contact between organisms and iron oxides (Munch & Ottow, 1982; Tugel et al., 1986; Forsythe et al. 1998); properties of the oxide, such as mineral form, crystallinity and particle size; sorption of Fe^{2+} ; biomineralization of Fe^{2+} , and the presence of organic ligands that enhance dissolution. This pathway of dissolution assumes the existence of “reductase” enzymes produced by the bacteria, but these enzymes have not been characterized so far. In addition there is the “shuttle system”, a new concept of electron transport which was suggested by Lovley and his coworkers. In this system, electrons are transferred by a range of compounds, which are not themselves modified, to the surface of the oxide. Among these compounds are cysteine, sulphide, U^{IV} and natural humics (Fig. 12.13; Lovley et al. 1996), as well as the synthetic humic acid analogues anthraquinone-2,6-disulphonate (AQDS) (Frederickson et al. 1998) and other quinones.

Enhancement of Fe oxide reduction by dissimilatory iron reducing bacteria (DIRB) under anoxic conditions was also observed and quantified in other systems. *Geobacter sulfurreducens* reduced ferrihydrite 8–11 times faster by using the cysteine/cystine system as an electron shuttle (Dong & Schink, 2002). Similarly, *Shewanella putrefaciens* reduced hematite up to fourfold faster in the presence of seven different kinds of natural organic matter (NOM; see p. 274) all of which acted as electron shuttles (Royer et al. 2002). The shuttle compound circulates between the microbially oxidized C-source which is the electron donor (acetate in Fig. 12.13) and the surface of the Fe-oxide which is the electron sink. This system is highly efficient because unlike a reducing agent which is oxidized upon reducing the Fe^{III} , the shuttle is not consumed; it is like a catalyst.

That the reduction takes place at the surface, receives support from an experiment in which the extent of reduction of various Fe oxides by *Shewanella alga* after 30 days was linearly correlated with the SA_{BET} ; the exception was 2-line ferrihydrite for which a surface area of $600 \text{ m}^2/\text{g}$ had to be assumed in order to fit the relationship (Roden & Zachara, 1996). Although experimental (BET) surface areas of ferrihydrite are substantially lower than $600 \text{ m}^2/\text{g}$, calculated values based on particle size as well as those determined from ligand adsorption experiments (see Table 5.1) are in this range. Dissolved Fe^{II} was found to create a lag phase in the reduction process (in contrast to the behaviour in inorganic systems) because Fe^{2+} is adsorbed at the cell surface (Liu et al. 2001). This effect can be overcome by complexing the Fe^{II} (e.g.

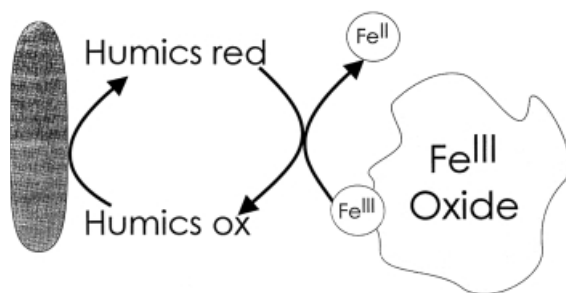


Fig.12.13 Humics, shuttelling electrons between Fe^{III} reducing bacteria and the surface of solid Fe^{III} oxide to produce dissolved Fe^{2+} (Lovley, 1997, with permission)

by NTA) or adsorbing it on Al_2O_3 or a clay mineral. It is suggested, therefore, that retardation is caused by the adsorption of the Fe^{II} at the the surface of the bacterial cells (Roden & Urrutia, 1999; Urrutia et al. 1999). The rate of reduction of goethite by *Shewanella alga* with lactate being the carbon source was proportional to the goethite surface area and to the lactate concentration; the free energy of this reaction was -22.7 kJ/mol lactate (Liu et al. 2001 a). Siderite was formed as a reduction product. As in inorganic systems, bacterial dissolution of goethite is also retarded by Al-substitution (Bousserrhine et al. 1999). On the other hand, Fe^{III} oxides, especially highly reactive ones, such as 2-line ferrihydrite ($\text{SA}_{\text{BET}} \sim 300 \text{ m}^2/\text{g}$), but not goethite ($15 \text{ m}^2/\text{g}$) or hematite ($8 \text{ m}^2/\text{g}$), prevented reduction of uranyl (U^{VI}) by *Shewanella alga* because they preferentially accepted the electrons (Wielinga et al. 2000).

Shewanella putrefaciens reduced synthetic and biogenic magnetite at pH 5–6 and 22–27 °C with formate or lactate as the electron donor (Kostka and Nealson, 1996). In this case electron transport was thought to require cell contact. Depending on the chemical composition of the aqueous phase, magnetite, green rust, siderite or vivianite are formed via solution around pH 7 (Fredrickson et al. 1998; Dong et al. 2000). In magnetite and green rust part of the Fe^{III} is sequestered and, thus, unavailable for anaerobic bacterial respiration. During microbially mediated, reductive dissolution of a ferrihydrite-coated sand held under dynamic flow conditions in a column, a proportion of the ferrihydrite was converted to goethite and magnetite (Benner et al. 2002).

The above reduction processes in *in vitro* systems were also observed in materials from soils, sediments and aquifers. This is environmentally relevant to the oxidative detoxification of a number of pollutants under anoxic conditions (see Chap. 21). An early example was the reduction of waterlogged marsh soil material (Brümmer, 1974) which was accompanied by a decrease in Eh and an increase in pH (eq. 12.10). The concentration of Mn^{2+} , Fe^{2+} and S^{2-} initially increased in this order until, at a later stage, precipitation of Fe^{II} sulphides caused $[\text{Fe}^{2+}]$ to drop (Fig. 12.14). This order is to be expected from the order of reducibility, but may be modified for kinetic reasons. For example, Peters and Conrad (1996) observed that sulphate was completely reduced in a range of aerobic soils *before* the Fe^{2+} concentration reached its maximum. They attributed this to the sluggishness with which reasonably well crystalline Fe oxides are reduced. This may also be the case where *Geobacter metallireducens* stimulated reduction of ferrihydrite *in vitro*, but failed to do so in aquifer material (Nevin & Lovley, 2000). In the presence of NO_3^- , biotic reduction of iron was delayed until all the NO_3^- and NO_2^- had been reduced (Jones et al., 1983); Jones et al. (1983) found that MnO_2 also suppressed reduction, whereas Tugel et al. (1986) observed little or no effect. As expected, addition of toluene or HgCl_2 (as bactericides), or pasteurization (Sørensen, 1982) completely blocked the reaction. A genus of acidophilic, heterotrophic species capable of reducing Fe oxides under strongly acidic conditions (pH 2–3) is *Acidiphilium* (Johnson & McGinness, 1991). The process is believed to start with reduction of the dissolved Fe^{III} ions which in turn induces further dissolution of Fe oxides by lowering the Fe^{III} activity in solution (Bridge & Johnson, 2000). This bacterium was found to be active in acid coal mine sediments where reduction was coupled with oxidation of glucose and a range of other carbon sources (Küsel et al. 1999; Küsel & Dorsch, 2000).

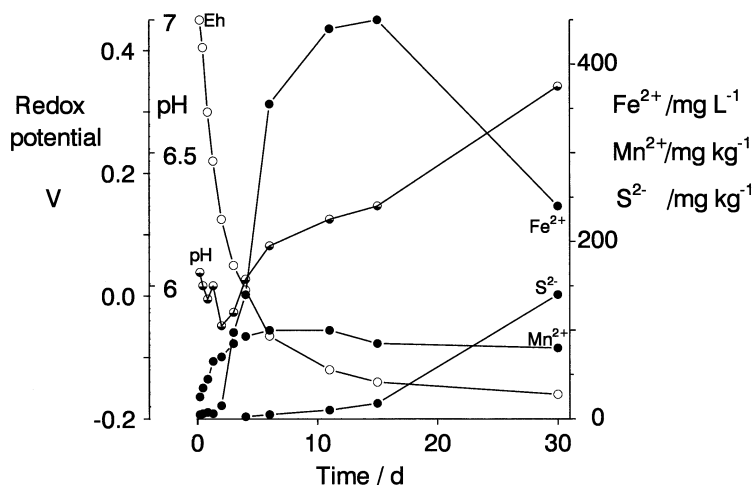


Fig. 12.14 Redoxpotential, pH and dissolved Fe^{2+} , exchangeable Mn^{2+} and monosulphide of a soil as a function of time after inundation (Brümmer, 1974, with permission).

Biological reductive dissolution by *Shewanella putrifaciens* of Fe oxides in material from four Atlantic pleistocene sediments (ca. 1.5–41 g/kg Fe oxides) was compared with that of the synthetic analogues (ferrihydrite, goethite, hematite) (Zachara et al. 1998). In the presence of AQDS as an electron shuttle, the percentage of bio-reduction of the three oxides was increased from 13.3%(fh); 9.2%(gt); and 0.6%(hm) to 94.6%; 32.8% and 9.9% with part of the Fe^{2+} formed being precipitated as vivianite and siderite, but not as magnetite. The quinone was reduced to hydroquinone which in turn, and in agreement with thermodynamics, reduced the Fe^{III} as it had much better access to the oxide surface than did the bacteria themselves.

In living organisms, the mobilization of iron from ferritin is of interest due to its physiological implications. *In vitro*, release of iron from ferritin can be achieved by chelation (slow) or by reductive dissolution. The kinetics of reductive dissolution of ferritin are related to the type and stability of the complexes formed at the surface of the iron hydroxide (Funk et al., 1985). An effective mobilizing agent *in vitro* is xanthine oxidase. Bolann and Ulvik (1987) showed that under aerobic conditions, the bulk of the iron released dissolved as a result of interaction of the iron core with a free radical $(\text{O}_2)^{\bullet}$ generated by the xanthine oxidase. Iron can also be removed reductively from ferritin by thioglycolic acid, dithionite and dihydroriboflavin 5'phosphate (Funk et al., 1985).

In natural environments, *abiotic* reduction may also be effected by a range of natural reductants including sulphide and methane. In the sulphide producing sediments in the Long Island Sound and the Mississippi Delta, for example, Fe oxides have been transformed to Fe^{II} sulphides (FeS and FeS_2) (Canfield & Berner, 1987; Boesen & Postma, 1988). As a result, when there was a sufficient supply of *reactive* Fe^{III} oxides in the sediments, hardly any dissolved sulphide was found in the pore water. The reduci-

bility of the different Fe oxides varied: of 10.75 mmoles of sulphide supplied, ferrihydrite consumed 8.83, lepidocrocite 9.37, goethite 2.71 and hematite 1.96 mmol in 4 h (Canfield, 1989), but such relationships may vary, depending on crystal size and structural order of the oxide. Methane is produced in strongly anaerobic environments, such as in flooded rice paddy fields and may become oxidized through reduction of Fe oxides. A column study using the lower layer of a rice soil showed that during oxidation of 0.36 mmoles CH_4 , 1.08 mmoles Fe^{III} were reduced (Miura et al., 1992). Soluble organic matter was also oxidized. Dissolution of ferrihydrite in the acidic vacuoles of marine protozoan grazers has been observed (Barbeau & Moffett, 1998).

12.2.5

Comparison of the three different types of dissolution reactions

There are only a few cases where the dissolution of an iron oxide by all three types of processes under comparable conditions has been investigated. Banwart et al. (1989) found that at pH 3, the rate of dissolution of hematite increased in the order, protonation < complexation < reduction with a factor of 350 between the extremes. A similar factor (400) was found for goethite (Zinder et al., 1986) (Fig. 12.15). Hematite dissolution processes were also compared in the pH range similar to that found in neutral environments (Fig. 12.16). Again, dissolution by simple protonation was extremely slow, whereas reduction, especially when aided by Fe^{III} complexing ligands, was particularly effective (Banwart et al., 1989). It can, thus, be concluded that reduction, particularly when assisted by protonation and complexation will be the main mechanism for Fe transport in global ecosystems.

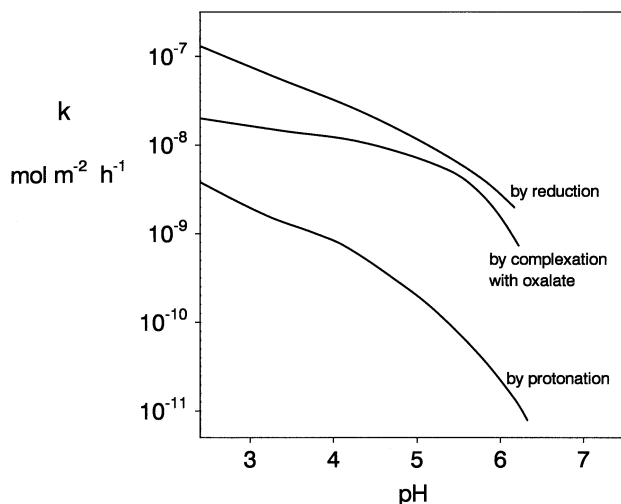


Fig. 12.15 Dissolution rate of goethite by protonation, complexation with oxalate and reduction by ascorbic acid as a function of pH (Stumm & Furrer, 1987, with permission).

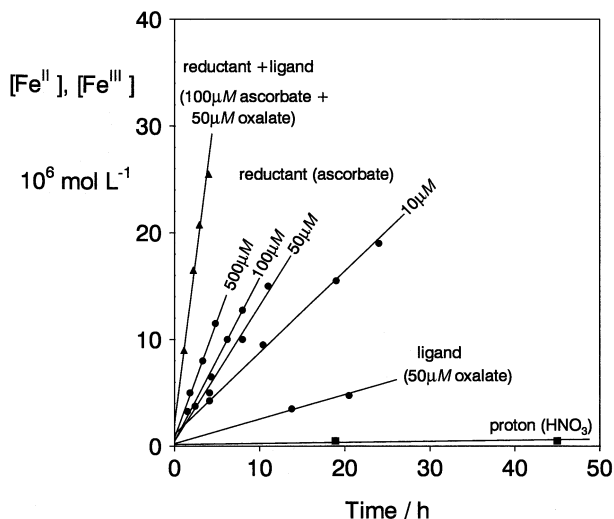


Fig. 12.16 Comparison of the dissolution of hematite at pH 3 by protonation (HNO_3), complexation ($50 \mu\text{M}$ oxalate), reduction ($100 \mu\text{M}$ ascorbic acid) and combined complexation-reduction (Banwart et al., 1989, with permission).

12.3

Dissolution equations

Information about the kinetics of dissolution reactions is provided by Delmon (1969) and by Brown et al. (1980). Dissolution may be either diffusion (i.e., transport) or surface controlled. If diffusion controlled, i.e., if the concentration of dissolved species immediately adjacent to the surface corresponds to the equilibrium solubility (c_e) of the solid phase, the concentration, c , of the dissolved species is diffusion controlled and increases with the square root of time, t , i.e.,

$$c = c_e + 2 kt^{1/2} \quad (12.12)$$

k being the rate constant. An example of this type of reaction is the very rapid dissolution of hematite by the tris (picolinate) V^{II} species; the chemical, i.e. surface-controlled, reaction is so fast that diffusion control predominates (Segal & Sellers, 1980, 1982). Another example is the acid leaching of iron oxides from bauxite which appears to be controlled by slow diffusion of acid through the pores created by the initial removal of the hematite (Patermarakis & Paspaliaris, 1989). In natural systems, transport-controlled dissolution may predominate in weathering environments where water movement is slow and the phase being dissolved is static. Dissolution reactions in which the chemical reaction at the solid/liquid interface is rate determining have an activation energy greater than 20 kJ mol^{-1} , whereas diffusion controlled reactions have lower activation energies. When investigating dissolution reac-

tions, it is essential to provide sufficient agitation to ensure that a contribution to the rate from diffusion control is avoided.

Table 12.2 lists a number of rate equations that are commonly applied to dissolution processes. Two equations that are used quite frequently are the cube rate law (Hixon & Crowell, 1931) which takes the geometry of the dissolving particle into account, and the Avrami-Erofejev law which applies to sigmoidal dissolution curves.

The cube root law is:

$$1 - (1 - \alpha)^{1/3} = kt \quad (12.15)$$

where α is the fraction of the solid dissolved at time t . The law applies to a situation in which the reaction interface moves inwards at a constant rate and implies isotropic dissolution, i.e., that the particle shape is maintained. It is also termed the shrinking core model and strictly speaking should apply only to spherical and cubic particles. It has, however, been applied successfully to the dissolution of goethite (Cornell et al., 1975; Sidhu et al., 1981; Chiarizia & Horwitz, 1991) and lepidocrocite (Cornell & Giovanoli, 1988a). Chiarizia and Horwitz (1991) also found that their data for dissolution of goethite in HCl, HNO₃ and H₂SO₄ could equally well be described by a first order law.

The Avrami-Erofejev law, i.e.,

$$(\ln(1 - \alpha))^{1/2} = kt \quad (12.16)$$

has been applied to dissolution of akaganéite (Cornell & Giovanoli, 1988a) and to hematite (Cornell & Giovanoli, 1993), both of which displayed sigmoidal dissolution curves. Another equation that has been applied to reactions with sigmoidal kinetics is the Kabai equation,

$$1 - \alpha = e^{-(kt)^a} \quad (12.17)$$

where a is a material constant ("constant of average order", Kabai, 1973). This equation provides a flexible way of summarizing experimental data, but does not provide a physical explanation for k and a . A relationship which expresses the rate of dissolution as a function of changing crystal size, morphology and site density (Christofferson & Christofferson, 1976; Postma, 1993) and also allows the effect of solution composition on rate to be separated from the effects due to changes in crystal morphology during dissolution, is

$$\frac{J}{m_0} = k \left(\frac{m}{m_0} \right)^\gamma \quad (12.18)$$

where J/m_0 is the normalized rate per initial mass of oxide (m_0), m is the mass dissolved at time t , k is the rate constant and γ is a material constant covering the change in properties during dissolution. This law was applied to dissolution data for

a series of Fe oxides with the order of dissolution being 2-line ferrihydrite > 6-line ferrihydrite = lepidocrocite > goethite (Larsen & Postma, 2001).

Gorichev and Kipriyanov (1984, and references therein) found that dissolution of powdered magnetite particles in HCl, H₂SO₄, H₃PO₄ and Na₂EDTA at temperatures of up to 80 °C displayed sigmoidal dissolution curves that could be described by,

$$-\ln(1 - \alpha) = A \cdot \sinh kt \quad (12.19)$$

For hematite and wüstite in the same media, the kinetic curves were deceleratory.

These dissolution models provide a summary of the dissolution reaction and its kinetics. Usually, the correlation coefficient, r^2 , for the relation between the measured values and those predicted by the model is taken as the criterion for the suitability of a particular model. Often, however, the very beginning or the very end of the dissolution curve is not included in the model – either because the data does not exist or because it does not fit; if only the middle data points – say 15–85% – are used, it is easy to get high r^2 values for several models. Although a model may provide some information about whether the rate determining step is the surface reaction or diffusion of the reacting species, the fact that a reaction follows a particular rate law does not guarantee that this describes the physical processes that take place. In some cases, an apparent rate law is the result of interaction between a number of counterbalancing processes. It should also be borne in mind that the shape of the kinetic curve and the extent to which a particular rate law is obeyed, are influenced by the particle size distribution of the sample. The broader the size distribution, the faster the initial stages of the reaction and the slower the latter part (Gallagher, 1965). The cube root law, for example, may be followed for up to 90% of the reaction by a monodisperse sample and up to only 60–70% of dissolution by the same material with a broad size distribution (Segal & Sellers, 1982).

12.4

Individual iron oxides

This section considers aspects and examples of the dissolution behaviour of individual iron oxides. Additional data are listed in Table 12.3 for a range of experimental conditions. As yet, characteristic dissolution rates cannot be assigned to the various iron oxides (Blesa & Maroto, 1986). There are, however, some consistent differences between oxides with considerable stability differences, hence a comparison of the oxides is included here. In addition, the reactivity of any particular oxide may vary from sample to sample, depending on its source (natural or synthetic) and the conditions under which it formed. To illustrate this, Table 12.4 summarizes conditions and results from dissolution experiments in which a range of samples of the same oxide was compared. How the properties of the sample influence its dissolution behaviour is still not fully understood. A thorough characterization of the samples by solid state analysis, e.g. by EXAFS, to provide a basis for understanding the dissolution behaviour is, therefore, desirable.

Tab. 12.4 Conditions and results from dissolution experiments comparing a range of samples of the same oxide

Oxide	Substitution	No. of samples	Surface area $\text{m}^2 \text{ g}^{-1}$	Dissolving medium	T (°C)	Model	Reaction rate	Activation energy (kJ mol^{-1})	Author
Gt nat	Al	10	24–169	6 M HCl	25	Kabai	$1 \cdot 10^{-2} - 1.7 \cdot 10^{-6} \text{ min}^{-1}$	–	Schwertmann, 1991
Gt syn	–	15	11–111	0.5 M HCl	10, 20, 40, 60	–	$0.03 - 0.75 \cdot 10^{-5} \text{ g Fe m}^{-2} \text{ h}^{-1}$ *	84–100	Cornell et al., 1974, 1976
Gt syn	–	7	14–111	0.5 M HCl	60, 100	cube root law	–	–	Cornell et al., 1975
Gt syn	–	14	13–153	6 M HCl	25	Kabai	$1 - 30 \cdot 10^{-3} \text{ min}^{-1}$	–	Schwertmann et al., 1985
Gt syn	Al	41	15–88	6 M HCl	25	Kabai	$0.10 - 15 \cdot 10^{-3} \text{ min}^{-1}$	–	Schwertmann, 1984 a & unpubl.
Gt syn	Al	8	147–228	1 M HCl	30, 40, 50	Kabai	$0.42 - 0.98 \cdot 10^{-3} \text{ min}^{-1}$ (30 °C)	68–91	Ruan & Gilkes, 1995
Gt syn	Al, Mn, Co, Ni, Cr	6	29–69	1 M HCl	40, 50, 60, 70	cube root law	$0.03 - 2.4 \cdot 10^{-2} \text{ g Fe g}^{-1} \text{ h}^{-1}$	40–120	Lim-Nunez & Gilkes, 1987
Gt syn	Al	3	62–88	oxalate, light	25	–	$0.136 - 0.150 \text{ mol H}^+ \text{ min}^{-1} \text{ m}^{-2}$	–	Cornell & Schindler 1987
Hm [§] syn	Al	4	171–230	1 M HCl	30, 40, 50	Kabai	$1.7 - 5.0 \cdot 10^{-3} \text{ min}^{-1}$ (30 °C)	66–69	Ruan & Gilkes, 1995
Hm [#] syn	Al, Mn, Co, Ni, Cr	6	–	1 M HCl	40, 50, 60, 70	–	$3.2 - 21.8 \cdot 10^{-2} \text{ g Fe g}^{-1} \text{ h}^{-1}$	–	Lim-Nunez & Gilkes, 1987
Hm ^{&} syn	Al, Mn, Co, Ni, Cr	6	–	1 M HCl	40, 50, 60, 70	–	$0.3 - 3.3 \cdot 10^{-2} \text{ g Fe g}^{-1} \text{ h}^{-1}$	–	Lim-Nunez & Gilkes, 1987
Hm syn	–	7	45–83	1 M HCl	65	Avrami-Erofejev	$1.8 - 7.3 \cdot 10^{-4} \text{ min}^{-1} \text{ m}^{-2}$	–	Cornell & Giovanoli, 1993

* initial rate in HCl at 20 °C

§ from goethites by heating at 240 and 260 °C

from goethites by heating at 300 °C

& from goethites by heating at 800 °C

12.4.1

Goethite**12.4.1.1 Unsubstituted goethite**

Dissolution of synthetic goethites in 0.5 M HCl at 20 °C indicated that the initial rate of dissolution per unit area ranged from $0.007\text{--}0.075 \cdot 10^4 \text{ g Fe h}^{-1} \text{ m}^{-2}$ and depended on crystal morphology (Cornell et al., 1974). The lowest dissolution rate/unit area was observed for the acicular crystals. Twinned crystals dissolved far more rapidly initially, because the twin boundaries acted as sites of preferential dissolution. Hematite centres of the epitaxial goethite twins were also preferentially dissolved. Data for complete dissolution of these samples followed the cube root law for up to 80–90% of the reaction (Cornell et al., 1975). Sigmoidal dissolution curves (6 M HCl, 24 °C) were obtained for acicular goethites grown in 0.3 M KOH at 4–70 °C and, therefore, having a range of crystallinities; the data could be fitted to both a modified Kabai equation (Schwertmann et al., 1985) and to the Avrami-Erofejev equation (Schwertmann, unpubl.) In all of the above investigations it was noted that although the acicular, multi-domainic crystals retained a basic needle-like shape for most of the reaction, dissolution was anisotropic. Initially the crystals became pointed at the domain ends. Subsequent preferential attack along the domain boundaries led to splitting off of single domains and diamond-shaped holes bounded by {210} faces also developed (Fig. 12.17).

These features led to a net increase in the surface area of the sample during the early stages of dissolution and this could explain the sigmoidal dissolution curve observed for some of the samples where the maximum in surface area coincided approximately with the maximum in dissolution rate, i. e. with the inflection point of the

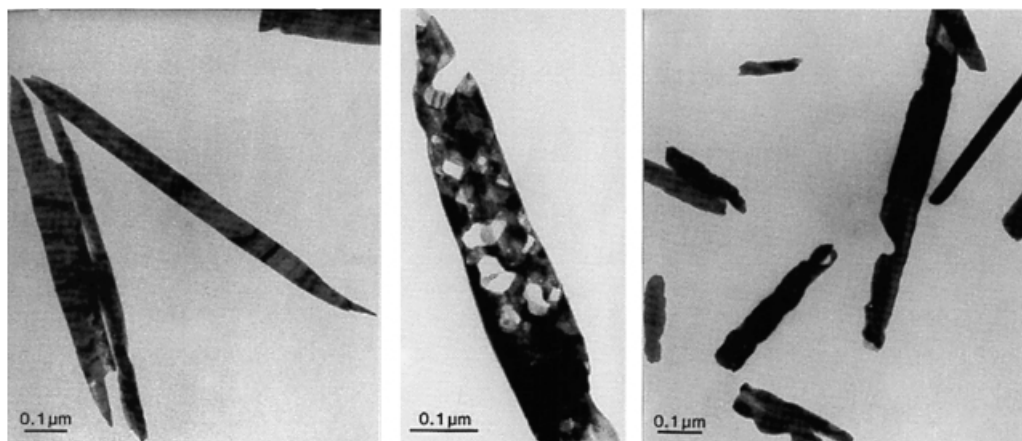


Fig. 12.17 Dissolution morphology of synthetic goethite crystals after partial dissolution in 6 M HCl at 25 °C. a) Pure goethite with dissolution along domain boundaries. b) Pure goethite with diamond-shaped dissolution holes bounded by

{210} faces. c) Monodomainic Al-goethite (Al/(Fe+Al) = 0.097 mol mol⁻¹) with cavous dissolution at crystal edges (Schwertmann, 1984 a, with permission).

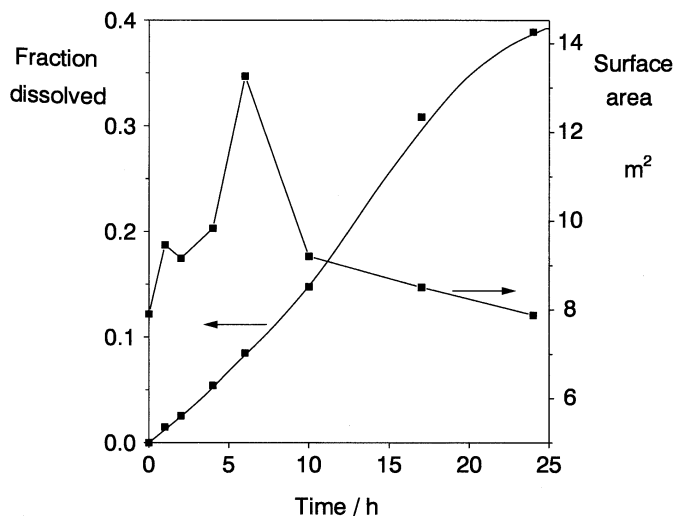


Fig. 12.18 Dissolved Fe and change of the sample's surface area with time during the dissolution of a synthetic goethite at 24 °C in 6 M HCl (Weidler, 1995, with permission).

dissolution curve (Fig. 12.18) (Weidler, 1995; Weidler et al. 1998). A deceleratory curve was obtained in earlier experiments probably because, due to the wide size distribution of the samples, complete dissolution of the smallest crystals outweighed the area increase due to development of holes in the larger crystals leading to a fortuitously continuous and smooth decrease in sample surface area (Cornell et al., 1975).

When the reaction conditions (temperature, acid concentration) are the same, dissolution rates of different samples depend on factors such as crystal size and surface area, Al substitution and crystallinity. As these factors are interrelated, it is often difficult to isolate the effect of any one of them. For example, the dissolution rate constant, k (min^{-1}) (Kabai equation) for a series of goethites grown at temperatures of between 4 and 70 °C and with surface areas of between 88 and 15 $\text{m}^2 \text{g}^{-1}$, respectively, increased from 0.001 to 0.030 min^{-1} as the synthesis temperature decreased. Similarly, there was a positive linear relationship between the dissolution (in 5M HCl at 20 °C) rate constant, $\ln k$, (Kabai) and SA for another series of goethites produced at between 5 and 90 °C (Strauss et al. 1997). Surface area is, however, not the only parameter to vary with sample synthesis temperature. The decrease in the unit cell edge length c from 0.4630 to 0.4609 nm, together with the increase in the separation of the two OH stretching vibrations ($\delta_{\text{OH}} - \gamma_{\text{OH}}$) from 93.8 to 96.6 cm^{-1} clearly indicated that internal order had increased which may have affected dissolution rate. Similar behaviour was noted for a hydrothermally grown series (125–180 °C) in which multi-domainic acicular goethites with highly serrated terminal edges were converted (“healed”) to monodomainic crystals with smooth edges (see Fig. 4.9) and the surface area thereby reduced from 88 to 30 $\text{m}^2 \text{g}^{-1}$ (at 180 °C). The acid dissolution rate constant dropped from 18 to $2.8 \cdot 10^{-3} \text{ min}^{-1}$ indicating that the crystals

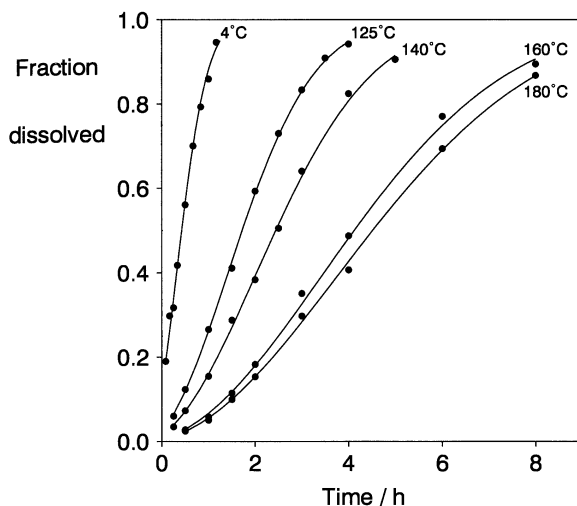


Fig. 12.19 Dissolution-time curves of a goethite synthesized at 4 °C in 0.3 M KOH before and after hydrothermal crystal “healing” at 125, 140, 160 and 180 °C for 16 h. The solid lines correspond to the Avrami-Erofejev model (Schwertmann et al. 1985, modified, with permission).

gained stability as a result of the hydrothermal treatment. The dissolution data fitted the Avrami-Erofejev model better than the Kabai equation (Fig. 12.19) which suggests that the suitability of a particular dissolution model may depend on crystal properties.

12.4.1.2 Substituted goethite

Figure 12.20 shows the dissolution curves for a set of Al-goethites grown from Al-ferrihydrite and containing up to 0.116 mol mol⁻¹ substitution. As Al substitution increases, the dissolution rate slows considerably and the shape of the curve becomes increasingly sigmoidal. The same effect was noted for Al-goethites produced by oxidation of Al containing FeCl₂ solutions (Fig. 12.21). The effect of substitution was more noticeable at higher dissolution temperatures (20–50 °C), but there was no clear relationship between level of substitution and activation energy (Ruan & Gilkes, 1995). This may reflect the fact that extent of Al substitution and other factors such as sample surface area and crystallinity are interrelated.

Al substitution (0.09–0.16 mol mol⁻¹) had no definite effect on the photochemical dissolution of substituted goethite in oxalate at pH 2.6 (Cornell & Schindler, 1987). On the other hand, Al substitution depressed the initial (linear) stage of dissolution of synthetic goethites and hematites in mixed dithionite/citrate/bicarbonate solutions (Fig. 12.22) (Torrent et al., 1987). As the variation in initial surface area has already been accounted for, the scatter of data in this figure is presumably due to variations in other crystal properties such as disorder and micropores. Norrish and Taylor (1961) noted that as Al substitution in soil goethites increased, the rate of reductive dissolution dropped (see also Jeanroy et al., 1991).

Other substituents also influence the dissolution rate. Of these, V^{III} and, in particular, Cr^{III} substantially stabilized goethite against proton attack, whereas the opposite effect was found for Mn^{III} (Fig. 12.23) (Schwertmann, 1991). Similar results were obtained by Lim-Nunez and Gilkes (1987). Unsubstituted and Cr-goethites had

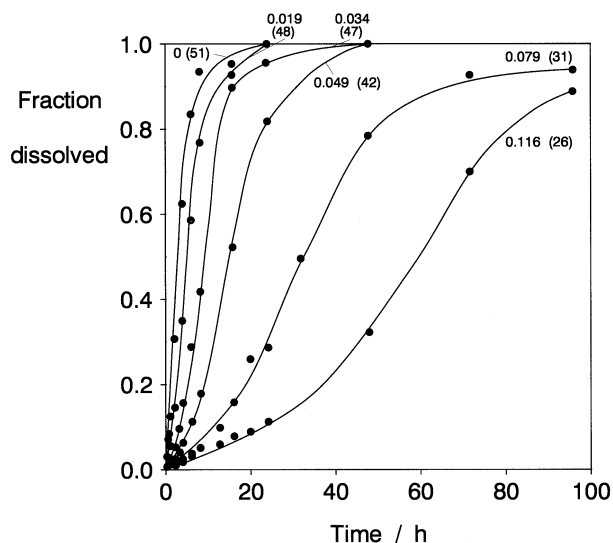


Fig. 12.20 Dissolution-time curves of synthetic Al substituted goethites in 6 M HCl at 25 °C. The figures at the curves indicate Al substitution expressed as Al/(Fe+Al) mol mol⁻¹ and the figures in () are surface areas in m² g⁻¹ (EGME) (Schwertmann, 1991, with permission).

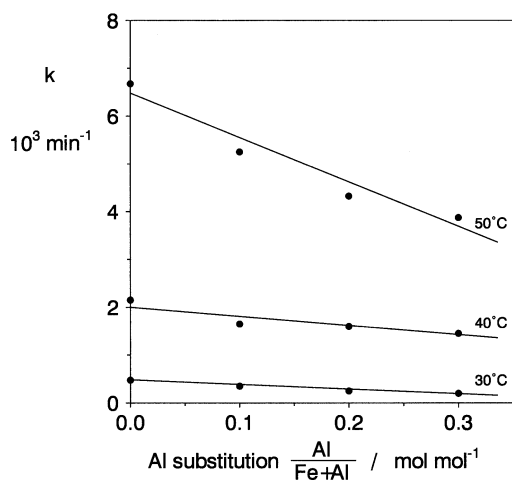


Fig. 12.21 Dissolution rate k (Kabai equation) in M HCl at 30, 40 and 50 °C versus Al substitution for Al-goethites produced by oxidation of mixed FeCl₂/AlCl₃ solutions (Ruan & Gilkes, 1995, with permission).

higher activation energies for acid dissolution (84–126 kJ mol⁻¹) than did Al-, Ni-, Co- and Mn-goethites (42–75 kJ mol⁻¹).

The effect of these substituents has not been fully explained. It is not, in most cases, due to formation of a protective layer of the substituent at the surface because M^{III} (M = trivalent substituent) and Fe^{III} usually dissolve congruently. Crystal defects (e.g. vacancies) created by substitution should accelerate dissolution, but this is not

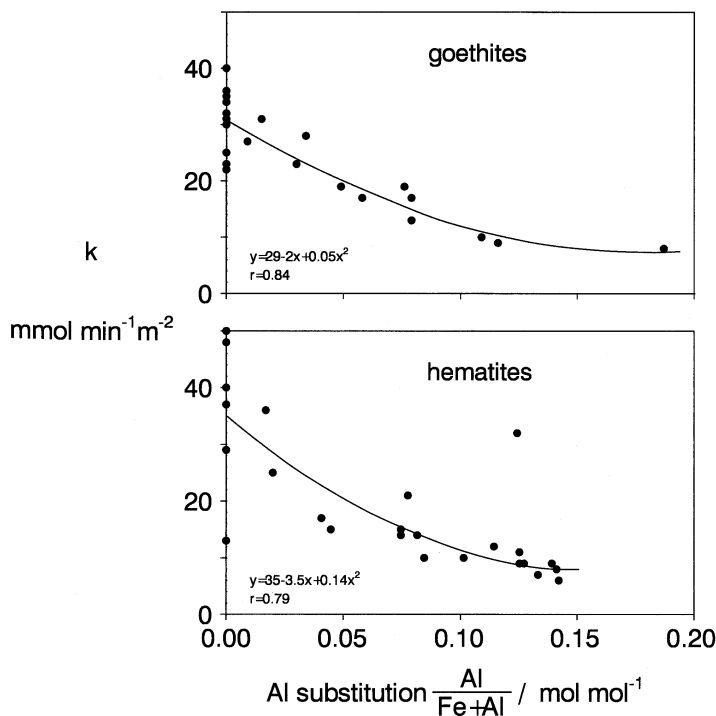


Fig. 12.22 Relationship between the dissolution rate per unit surface area in Na-dithionite/citrate/bicarbonate at 25 °C and the Al substitution of 28 synthetic goethites (upper) and 24 synthetic hematites (lower) (Torrent et al., 1987, with permission).

the case for V, Al and Cr. Apparently bond strength has a deciding influence with the M-OH...OFe or M-O-Fe bonds being stronger than pure Fe-O bonds and thus more resistant to protonation. Support for the importance of bond strength comes from IR data. The difference between the two OH bending modes (δ_{OH} at ca. 800 cm⁻¹ and γ_{OH} at ca. 900 cm⁻¹) increased with increasing Al and Cr substitution (but not V) and as dissolution proceeded, crystals with a higher ($\delta_{\text{OH}} - \gamma_{\text{OH}}$) difference accumulated which indicates their greater resistance to proton attack (Schwertmann, 1984a). The high resistance of Cr-substituted goethite may also be connected to the very low rate of H₂O exchange of Cr^{III} (Burgess, 1988). In contrast, Mn-goethites showed a decrease in ($\delta_{\text{OH}} - \gamma_{\text{OH}}$) (Stiers & Schwertmann, 1985) and dissolved more rapidly than pure goethite (Fig. 12.23). To the best of our knowledge, no experiments with the structural MOOH analogues are available to date.

12.4.1.3 Natural goethite and hematite

Leaching of ores, i.e. the separation of Fe oxides from silicate minerals has prompted investigations into the acid dissolution behaviour of natural goethites and hematites (Surana & Warren, 1969; Warren & Roach, 1971). Dissolution curves

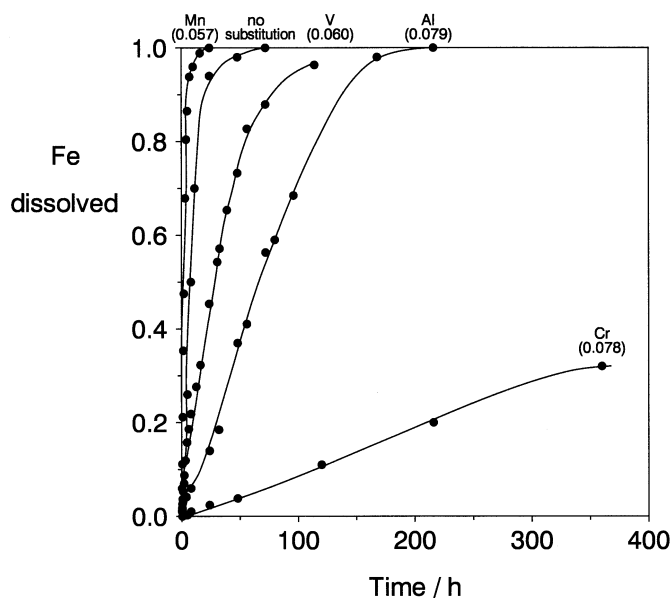


Fig. 12.23 Dissolution-time curves for metal (M)-substituted goethites ($M/(Fe+M)$) as compared to pure goethite without substitution; Mn^{3+} (0.057); V^{3+} (0.060); Al^{3+} (0.079); Cr^{3+} (0.078) (Schwertmann, 1991 and unpubl., with permission).

of natural crushed goethite were usually sigmoidal with the ratio of dissolution rate in 2 M $HClO_4$, H_2SO_4 and HCl being 1:5:20 (Surana & Warren, 1969): the activation energy for dissolution in the three acids was 74.6, 83.4 and 94.3 kJ mol^{-1} , respectively. The rate was approximately first order with respect to $[H^+]$. In the presence of SO_2 , increasing P_{SO_2} accelerated the dissolution process. The crystal surface became deeply pitted as the reaction proceeded and this was considered to have caused the initial acceleration of the dissolution process. The cause of pitting was not determined. Chloride, sulphate and bisulphite anions accelerated the reaction; these ions adsorbed forming surface Fe complexes, thereby facilitating the detachment of iron.

The data for dissolution in HCl of a range of natural goethites from tropical soils and also of so-called lake iron ores with widely varying crystallinities and degrees of Al substitution could be fitted to the Kabai equation (Tab. 12.5) (Schwertmann, 1991). The great differences in dissolution rate could not be explained satisfactorily in terms of surface area, MCL_{011} or Al substitution, although a trend towards slower dissolution was observed as structural Al increased. The poorly crystalline goethite/ferrihydrite mixtures from the Finnish lake ores had rate constants of $0.17-1.7 \cdot 10^{-3} \text{ min}^{-1}$ in 2 M HCl which showed a positive correlation with the ratio Fe_o/Fe_d and indicated that the ferrihydrite fraction dissolved faster than did the goethite (Schwertmann et al., 1987).

Tab. 12.5 Properties of soil goethites and their dissolution rates in 6 M HCl at 25 °C

<i>Goethite source</i>	<i>Fe content g kg⁻¹</i>	<i>Al/(Fe + Al) mol mol⁻¹</i>	<i>MCL₁₀₁ nm</i>	<i>Surface area* m² g⁻¹</i>	<i>Dissolution rate[§] k/min⁻¹</i>
Oxisol, New Caledonia	385	0.04	14	129	$5.50 \cdot 10^{-3}$
ditto	487	0.03	20	169	$8.51 \cdot 10^{-3}$
ditto	483	0.07	30	79	$0.42 \cdot 10^{-3}$
ditto	228	0.13	25	96	$1.66 \cdot 10^{-7}$
ditto	n.d. #	0.05	18	121	$1.95 \cdot 10^{-3}$
Saprolite, S. India	144	0.11	75	24	$3.09 \cdot 10^{-4}$
Saprolite, S. Brazil	196	0.22	27	87	$9.33 \cdot 10^{-5}$
Saprolite, S. Brazil	117	0.16	14	n.d.	$6.92 \cdot 10^{-3}$
Lake ore, Finland	–	0.0	13	142	$1.07 \cdot 10^{-2}$
Concretion, S. India	535	0.06	15	54	$8.71 \cdot 10^{-5}$

§ Kabai model (1973)

* EGME

n.d. = not determined

12.4.2

Lepidocrocite and akaganéite

Only a few investigations of the dissolution of lepidocrocite or akaganéite have been carried out. Being thermodynamically less stable than goethite or hematite, lepidocrocite dissolves more rapidly than either of these compounds. This was demonstrated for dissolution in strong acids (Sidhu et al., 1981; Cornell & Giovanoli, 1988a), H₂S (Canfield, 1989; Dos Santos Afonso & Stumm, 1992), mugineic acid (Inoue et al., 1993; Hiradate & Inoue, 1998) and in H₂ (Fischer, 1987).

The dissolution of lepidocrocite in 0.5 M HCl at 76 °C was deceleratory and the data fitted the cube root law for around 80% of the reaction (Cornell & Giovanoli, 1988a). TEM showed that the crystals maintained their lathlike shape for the bulk of the reaction by dissolving preferentially at the edges which became strongly corroded. Except at domain boundaries or at surface imperfections where holes similar to those observed for goethite developed, the acid attack at the main (001) face appeared to be slight. During the dissolution in KOH of highly serrated lepidocrocite crystals (see Fig. 4.14b) the domainic outgrowths were the first to dissolve leading to blunted edges. In a second step, terraced edges formed parallel to [100] and finally the elongated crystals turned into small cubes. This was accompanied by formation of acicular goethite which acts as a sink for the dissolved iron (Schwertmann & Taylor, 1972a).

Dissolution curves for akaganéite in 0.5 M HCl at 76 °C were sigmoidal. TEM showed that acid attack was concentrated along the [001] direction; initially the tapered ends of the spindle-shaped crystals (see Fig. 4.15a) became squared and, as dissolution continued, the crystals became shorter (Fig. 12.24a–c). With further dissolution the crystals were gradually hollowed out (Fig. 12.24d) and it is the resulting increase in surface area that is thought to be responsible for the shape of the dissolution curve (Cornell & Giovanoli, 1988a).

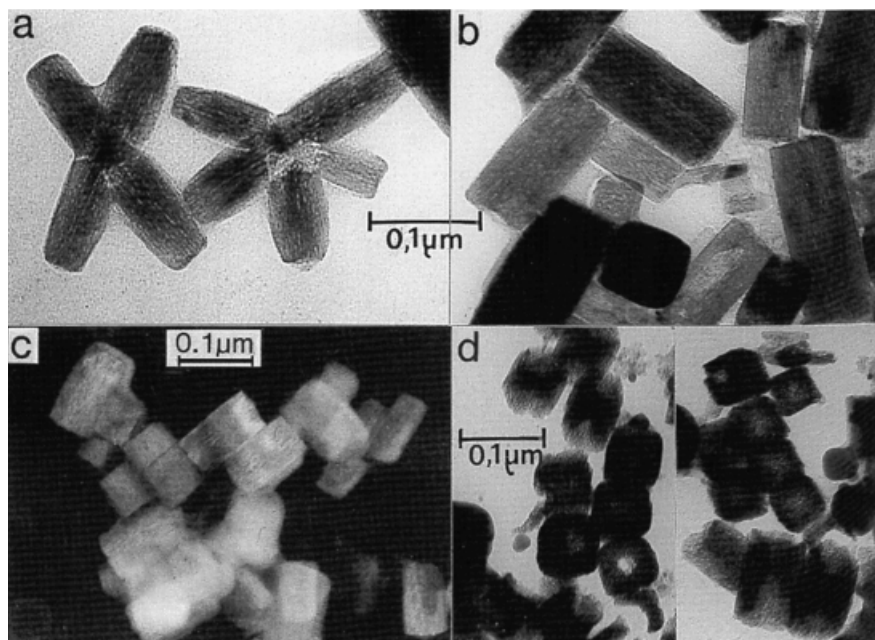


Fig. 12.24 Morphological changes of somatoidal akaganéite crystals after a) 10; b) 25; c) 50, Cr-shadowed; and d) 80% dissolution (Cornell & Giovanoli, 1988 a, with permission).

12.4.3

Ferrihydrite

Although 2-line ferrihydrite has been used for dissolution studies, 6-line ferrihydrite has, to date, not been investigated. Fischer (1976) compared the dissolution behaviour of three 2-line ferrihydrites in 0.2 M oxalate and found the slowest dissolution rate for a slowly precipitated sample and faster dissolution for rapidly precipitated samples (hydrolysed by fast addition of NH_3 or by bacterial oxidation of Fe^{III} citrate). Adsorbed silicate reduced the dissolution rate in oxalate probably by blocking surface Fe sites (Schwertmann & Thalmann, 1976).

A method used for soils and other geomaterials is the semiquantitative separation of ferrihydrite from better crystalline Fe oxides, especially goethite and hematite, by a single extraction with acid oxalate solution in the dark (Schwertmann, 1959, 1964; McKeague & Day, 1966; Campbell & Schwertmann, 1985; Schwertmann, 1991) (see also 7.11). This method is based on the significantly different dissolution rates (1–2 orders of magnitude) between ferrihydrite and the other, more stable oxides. In general, the greater the differences with respect to crystallinity, the sharper the separation. Although in many synthetic systems these differences are very great – for example, in a system where a 2-line ferrihydrite transforms to goethite or hematite (see Chap. 14) – differences between Fe oxides in natural materials are often less

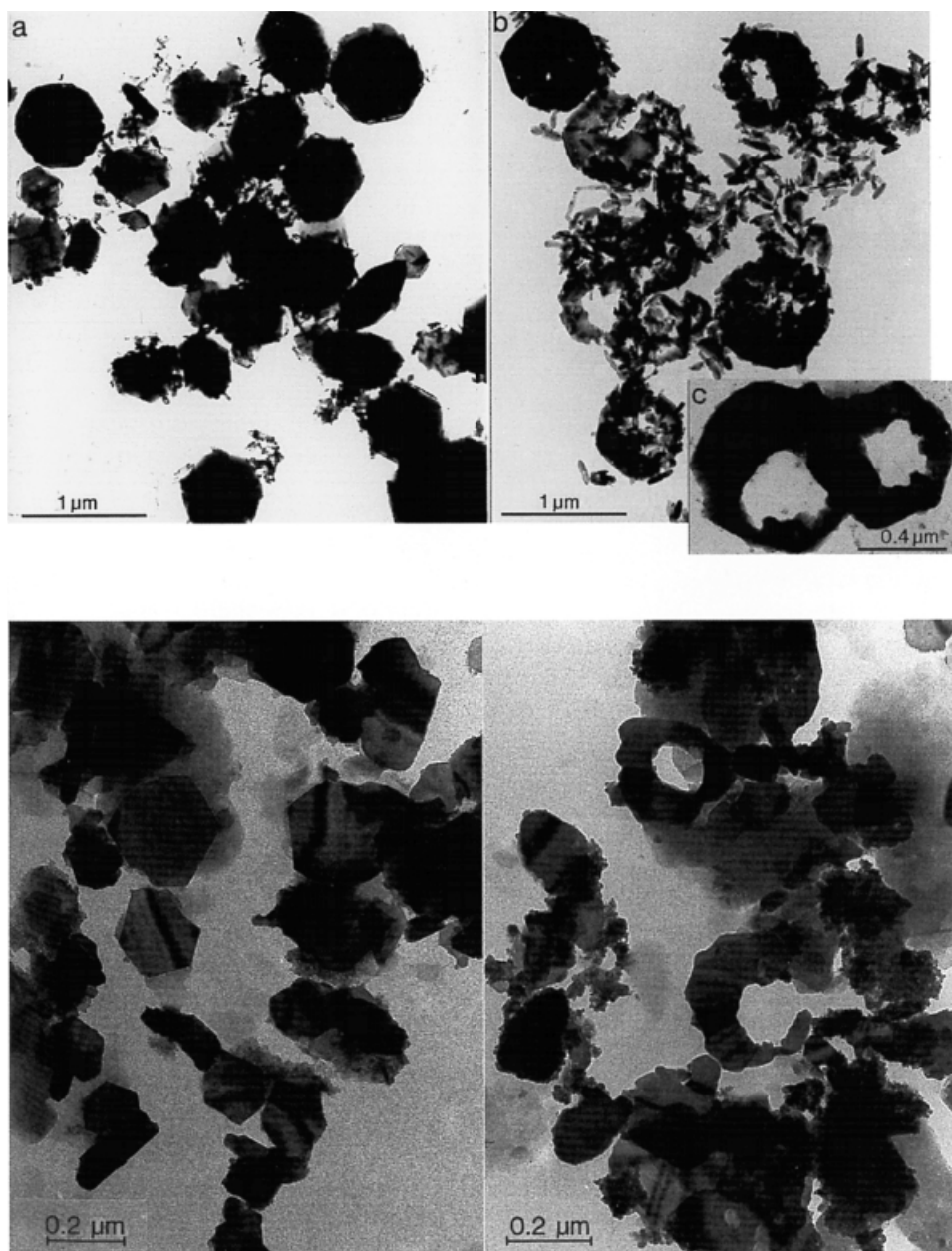


Fig. 12.25 Dissolution features of hematites: Upper: Undissolved (a) and partly dissolved (b; c) synthetic Al-hematite ($\text{Al}/(\text{Fe} + \text{Al}) = 0.094 \text{ mol mol}^{-1}$) in dithionite/citrate/bicarbonate at 25°C (Araki & Schwertmann unpubl.), Lower: Undissolved and partly dissolved hematite from a redoxomorphic subsoil of a typical Hapludalf on Permian mudstone, Ohio (Bigham et al., 1991, with permission).

and so their separation is not so precise. Magnetite, for example, may dissolve to some extent in oxalate. Furthermore, although most of the ferrihydrite is already dissolved in the first 15 min (Fischer, 1976) some better crystalline or Si-containing ferrihydrite may need more than 2 h of extraction while at the same time other oxides, in particular, fine grained lepidocrocite, will also start to dissolve (Schwertmann, 1973; Wang et al., 1993).

Nevertheless, the so-called oxalate method i.e. a two hour extraction with 0.2 M oxalate at pH 3 and RT is now being widely used in soil research and beyond (Schwertmann, 1984b). It was originally proposed by Tamm (1922, 1932). Later it was found that light has to be excluded to guarantee the separation (Schwertmann, 1964) because in the presence of light, goethite and hematite will also dissolve by photochemical reduction. After ferrihydrite had been recognized as a separate phase, it was shown by differential X-ray diffraction that it was this phase which dissolved preferentially. Ferrihydrite-goethite associations, common in soils, exhibited a break in their dissolution-time curves in oxalate, usually at around 2–4 hours which reflects the transition from a fast dissolution of ferrihydrite to a slower dissolution of goethite (Schwertmann et al., 1982).

12.4.4

Hematite

Dissolution vs. time-curves for acid dissolution (M HCl, 65 °C) of synthetic hematites with a range of morphologies (platy, diamond shaped, ellipsoidal, acicular and sub-rounded) were sigmoidal; the data fitted the Avrami-Erofejev equation (Cornell & Giovanoli, 1993). The dissolution rate was linearly related to the initial surface area of the samples, but a lower rate per unit area was found for solution-grown hematite than for that produced by heating of goethite at > 600 °C. This difference is probably due to a higher proportion of structural defects being produced at high temperatures. For most morphologies, dissolution was shape-preserving and there appeared to be no preferential attack at any particular crystal face (Cornell & Giovanoli, 1993). Central holes developed on the basal faces (001) of the platy crystals; these were probably the result of enhanced dissolution at screw dislocations as happens with natural hematite crystals (Sunagawa, 1962a). Similar hole formation has been noted during reductive dissolution with dithionite (Fig. 12.25b,c) and during microbial reduction in anaerobic soils formed on hematitic parent material (Fig. 12.25 lower right) (Bigham et al., 1991). Rod-like crystals bounded by prismatic faces and formed by growth from a central nucleus in both directions along the *c*-axis, developed an hourglass shape as after partial dissolution in acid (Cornell, 1985). Enhanced proton attack occurred in the vicinity of the original hematite nucleus because this was surrounded by a region of strain.

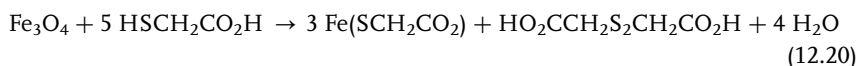
The rate of reductive dissolution of monodispersed hematite by ascorbic acid (up to $0.5 \cdot 10^{-4}$ M, 25 °C) increased with increasing coverage by adsorbed ascorbate from 2.4 min^{-1} at pH 4 to 6.6 min^{-1} at pH 3 (Suter et al., 1991). Al substitution depressed the rate of reductive dissolution of hematite (Fig. 12.22) (Torrent et al., 1987). The scatter of the data was large and could not be accounted for by variations in other properties of the samples. Cu substitution ($0.09 \text{ mol mol}^{-1}$) did not influ-

ence the rate of acid dissolution of hematite; Cu release was congruent (Cornell & Giovanoli, 1993). Phosphorous-containing hematites (up to 0.03 mol mol⁻¹), produced at 100 °C, showed congruent dissolution in 8.75M HCl/0.875M H₂SO₄ at 25 °C (indicating structural incorporation of P) with their half-dissolution time increasing from ca. 25 to 140 min as the P content increased (Galvez et al. 1999). Chromium (3.5–12.5 wt%) stabilized hematite against dissolution in a citric acid-EDTA-ascorbic acid mixture (Joseph et al. 1999).

12.4.5

Magnetite and maghemite

Magnetite (Fe^{II}Fe^{III}₂O₄) usually dissolves faster than the pure Fe^{III} oxides due both to its Fe^{II} content and also because Fe^{III} occurs in octahedral and tetrahedral positions. Bruyere & Blesa, (1985) have reviewed dissolution studies in mineral acids. In a series of papers, Blesa and coworkers also reported on the dissolution behaviour of magnetite and maghemite under complexing and reducing conditions (Tab. 12.3). In thioglycolic acid the rate of dissolution of magnetite (10 m² g⁻¹) increased progressively from 0.4 to 1.6 · 10⁻⁴ s⁻¹ as the acid concentration rose from 0.03 to 0.72 M. The rate was linearly related to sample surface area and was at a maximum at between pH 4–5 (Baumgartner et al., 1982). Thioglycolic acid forms strong complexes with both Fe^{II} and Fe^{III} and reduces the latter by intramolecular electron transfer. The dissolution reaction can be written as (Leussing & Kolthoff, 1953),



Polyelectrolytes such as Na polyacrylate, polymethylacrylate and polystyrene sulphonate which form multiple site, surface complexes, strongly retarded dissolution and this effect was attributed to blocking of the surface sites by adsorption of these compounds (Baumgartner, 1985).

Dissolution of magnetite in EDTA-Fe^{II} solution has been followed by titration of the protons formed by oxidation of Fe²⁺ with KNO₃ (Blesa et al., 1984; Borghi et al., 1989). The rate of dissolution in EDTA alone was very slow due to formation of stable EDTA-Fe surface complexes which hindered detachment of structural Fe. In the presence of dissolved Fe²⁺, however, dissolution was accelerated significantly, because the rate determining electron transfer from an Fe^{II}-EDTA complex to an Fe^{III}-EDTA surface complex is facilitated by the higher stability of the Fe^{III} complex over the Fe^{II} complex. The reaction was inhibited if EDTA was in excess of Fe^{II} owing to competitive adsorption of EDTA and the Fe^{II}-EDTA complex. Similar rapid dissolution was observed in nitrotriacetatoferrate/Fe²⁺ (Del Valle Hidalgo et al., 1988) and in oxalate/Fe²⁺ (Blesa et al., 1987) where at 30 °C, the initial rate was a linear function of [Fe²⁺] and a rate maximum was found at pH 3. Partial replacement of Fe^{II} in the magnetite structure by Co^{II} to give Co_xFe_{3-x}O₄, did not affect the rate of dissolution in thioglycolic acid at x = 0.50, but lowered the rate at x = 0.69, probably as a result of a change in the electronic structure of the oxide surface (Blesa et al., 1986).

A study of dissolution of large, single crystals of magnetite by V^{II} in the form of V^{II} -picolinate is one of the few examples where the solid phase as well as the solution was characterized (Allen et al., 1988). The dissolution rate was crystal face specific with $\{110\} < \{100\} < \{111\}$: the rates were 0.34, 0.58 and 0.91 g m⁻² min⁻¹, respectively. The most common form (see Chap. 4), the $\{111\}$, appears to be the most sensitive to reductive dissolution; etch pits bounded by $\{110\}$ walls occurred most frequently on $\{111\}$. Surface spectrographic measurement (XPS and Auger) and Mössbauer spectroscopy indicated a hydroxylated surface and demonstrated preferential dissolution of octahedral Fe^{III} which led to a complete breakdown of the structure. In spite of some etch pit formation (Allen et al., 1988), the overall dissolution of magnetite appears to be shape preserving, at least to the extent that dissolution can be modelled with the cube root law. Overall shape preservation is also indicated by TEM observations (Sidhu et al., 1981). *In situ* ellipsometry combined with XRD and TEM showed that during dissolution in HCl, magnetite films on steel scaled off the substrate in small pieces during the entire reaction. When, however, the oxide films contained ca 10% hematite, the whole film lifted off the underlying steel in one piece at the end of the dissolution process (Bjorklund et al. 1998)

Photochemical reductive dissolution of *maghemite* in the presence of ligands (L) such as EDTA, thiocyanate and oxalate has been documented by Litter and Blesa (1988, 1990, 1992) and Litter et al. (1991). Dissolution of commercial maghemite in 10⁻² M EDTA (pH 2) was greatly accelerated if irradiated with light of $\lambda = 254$ or 366 nm, whereas light of $\lambda = 450$ nm was ineffective. Formaldehyde was identified as an oxidation product of the EDTA indicating that EDTA supplies electrons for reduction of surface Fe^{III} as well as to Fe^{III} -L complexes. This process accelerates maghemite dissolution. In contrast to oxalate and EDTA, thiocyanate was ineffective owing to its low affinity for the oxide surface.

12.4.6

Comparison of different oxides

As stated before, there is no fixed dissolution rate for a given mineral-specific structure, because rate-determining factors can vary significantly for different samples of the same oxide. Nevertheless, some consistent mineral-specific differences from studies comparing different oxides have evolved.

Such comparisons have been made for all three types of dissolution reactions. In strong acids ferrihydrite dissolved much faster than goethite and hematite, the difference being around three orders of magnitude (Cornell et al., 1974). A similar order (ferrihydrite $\gg$ hematite $>$ goethite) was also found in oxalate at pH 3 and 5 (Fig. 12.2). For the better crystalline oxides, Sidhu et al. (1981) found dissolution time curves depicted in Figure 12.26. The corresponding data for the initial rate, the activation energy and the frequency factor are given in Table 12.6. The rate follows the order goethite $<$ hematite $<$ maghemite $<$ akaganéite $<$ magnetite $<$ lepidocrocite. Lower dissolution rates (in HCl) for goethite than for hematite were also found by Cornell and Giovanoli (1993).

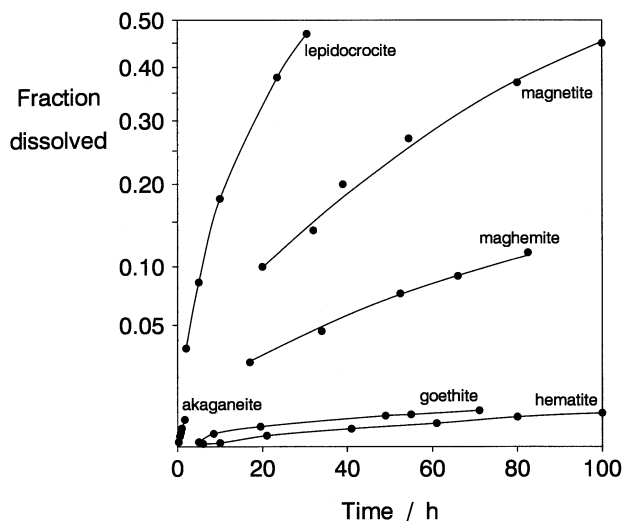


Fig. 12.26 Dissolution-time curves for various Fe oxides in 0.5 M HCl at 25 °C (Sidhu et al., 1981, with permission).

Tab. 12.6 Average dissolution rate, activation energy and frequency factor for the dissolution of various iron oxides in 0.5 M HCl at 25 °C (Sidhu et al., 1981).

Mineral	Dissolution rate k $10^4 \text{ g Fe m}^{-2} \text{ h}^{-1}$	Activation energy $E_a^\S$ kJ mol^{-1}	Frequency factor $A^\S$ (Fe dissolved/ $\text{g m}^{-2} \text{ h}^{-1}$)
Goethite	0.05	94	$3.0 \cdot 10^{11}$
Lepidocrocite	6.43	84	$5.8 \cdot 10^{11}$
Akaganéite	1.40	67	$7.4 \cdot 10^7$
Hematite	0.13	88	$2.1 \cdot 10^{10}$
Magnetite	3.48	80	$1.8 \cdot 10^{10}$
Maghemite	0.99	85	$5.1 \cdot 10^{10}$

$\S \quad k = A e^{\frac{-E_a}{RT}}$

Although goethite and hematite have similar thermodynamic stabilities, their dissolution rates relative to each other may vary. For example, for reductive dissolution in 10 mM ascorbic acid at pH 3 the order was: ferrihydrite $\gg$ goethite > hematite (Postma, 1993) (Fig. 12.27). The reversed behaviour of goethite and hematite appears to be partly due to their difference in surface area. A comparison of the rates in ascorbic acid from various authors (at an ascorbic acid concentration sufficiently high to saturate the surface of the oxides) (Postma, 1993) gave the following initial dissolution rates ($\text{mol m}^{-2} \text{ s}^{-1}$): ferrihydrite ($339 \text{ m}^2 \text{ g}^{-1}$): $1.2 \cdot 10^{-8}$ (Postma, 1993); hematite ($17.5 \text{ m}^2 \text{ g}^{-1}$): $6.1 \cdot 10^{-11}$ (Banwart et al., 1989) and goethite ($19 \text{ m}^2 \text{ g}^{-1}$): $1.8 \cdot 10^{-11}$ (Zinder et al., 1986). Again there is a factor of ca. 10^3 between ferrihydrite and the other two oxides. In hydroquinone at pH 1.9–13.8 much faster reductive dissolution

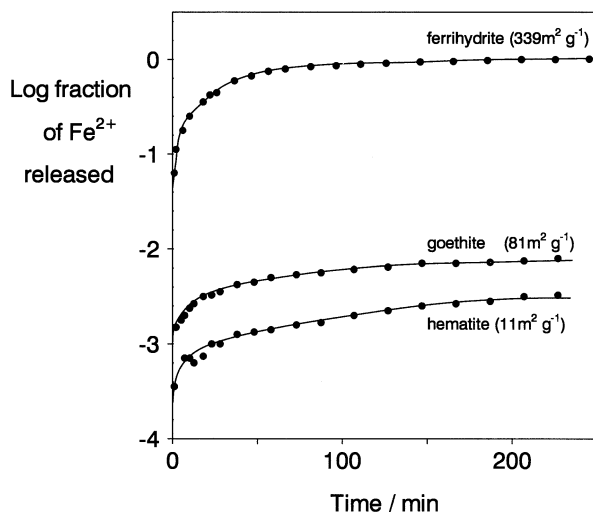


Fig. 12.27 Dissolution-time curves for synthetic ferrihydrite, goethite and hematite in 10 mM ascorbic acid at pH 3 (Postma, 1993, with permission).

of goethite over that of hematite was noticed by LaKind and Stone (1989) (factor of 10^2 at pH 3.4). This was attributed to goethite's lower density (4.37 vs. 5.26 g cm⁻³) and its double rows of empty octahedral sites (see Chap. 2). The surface area was only given for goethite (44 m² g⁻¹), but the monodisperse hematite had 1 μ m sized particles, i. e. a much lower surface area, which may also have been important.

Figure 12.28 compares the reductive dissolution of synthetic magnetite, maghemite and hematite in 0.02 M EDTA in the presence of UV light or Fe²⁺ at pH 3.0 and 30° C. The rates (10^7 s⁻¹ cm⁻²) were 2.3; 1.2 and 0.0063 for the three oxides, respectively, clearly demonstrating the very low dissolution ability of the corundum-structured oxide (hematite) as against that of the spinel-structured oxides. The authors attributed this to higher electron mobility in the spinel structure (Litter & Blesa, 1992). With sulphide as a reductant, ferrihydrite and lepidocrocite were significantly more reactive than goethite and hematite (Canfield, 1989) (Tab. 12.7). This process is relevant to the sulphide produced microbially in coastal sediments, leading to the formation of Fe^{II} sulphides.

Dos Santos Alfonso and Stumm (1992) suggested that the rate of reductive dissolution by H₂S of the common oxides is a function of the formation rate of the two surface complexes =FeS⁻ and =FeSH. The rate (10^7 mol m⁻² min⁻¹) followed the order lepidocrocite (20) > magnetite (14) > goethite (5.2) > hematite (1.1), and except for magnetite, it was linearly related to free energy, ΔG_r^0 , of the reduction reactions of these oxides (see eq. 9.24). A factor of 75 was found for the reductive dissolution by H₂S and Fe^{II} sulphide formation between ferrihydrite and goethite which could only be explained to a small extent by the difference in specific surface area (Pyzik & Sommer, 1981).

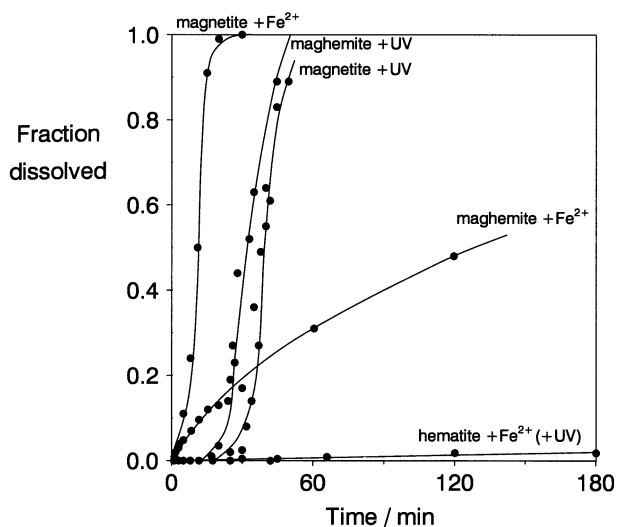


Fig. 12.28 Dissolution-time curves for magnetite, maghemite and hematite in EDTA at 30 °C and pH 3 in the presence or absence of Fe^{2+} and UV light ($\lambda = 254 \text{ nm}$) (Litter & Blesa, 1992, with permission).

Tab. 12.7 Sulphide remaining after reaction of 11 mmol sulphide with various synthetic Fe oxides for 4 h at RT (Canfield, 1989; with permission).

<i>Fe oxide</i>	<i>Sulphide remained/ mmol</i>
Goethite	8.04
Lepidocrocite	1.38
Ferrihydrite	1.92
Hematite	8.79
Control	10.75

Tab. 12.8 Per cent reduction of three Fe oxides by *Shewanella putrefaciens* in the absence (–) and presence (+) of anthraquinone-2,6-disulfonate (AQDS) (Zachara et al. 1998).

<i>Oxide</i>	–	AQDS
Ferrihydrite	13.4	94.6
Goethite	9.2	32.8
Hematite	0.6	9.9

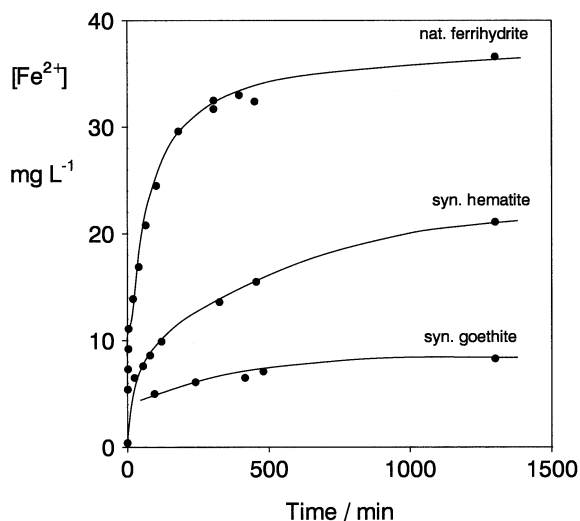


Fig. 12.29 Reduction-time curves of various Fe oxides by *Corynebacteria* during anaerobic incubation (Fischer, 1987, with permission).

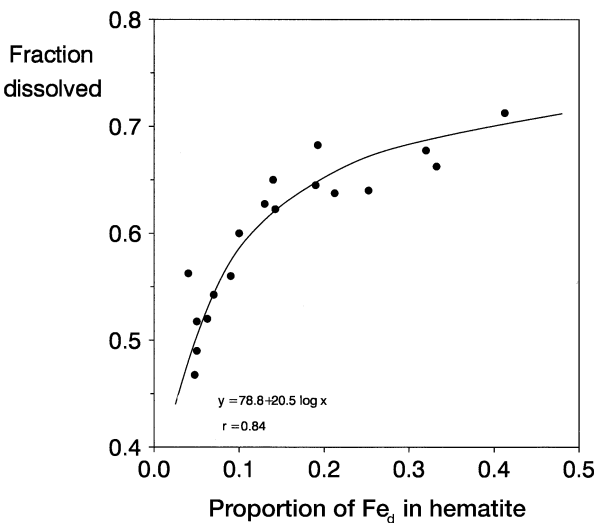


Fig. 12.30 Relationship between the fraction of oxidic Fe dissolved by dithionite/citrate/bicarbonate in 30 min and the proportion of Fe in hematite in hematitic/goethitic clay fractions of some Spanish soils (Barrón & Torrent, 1987, with permission).

The rate of the biotic reduction of Fe oxides by a strain of *Corynebacterium* under O₂-free conditions followed the order: natural ferrihydrite $\gg$ synthetic goethite > hematite (Fischer (1988) (Fig. 12.29) in accordance with the sequence in reducibility by Fe-reducing bacteria isolated from a eutrophic lake sediment (Jones et al., 1983). Iron from ferrihydrite reduced by *Shewanella alga* was found to be isotopically lighter than that of the ferrihydrite Fe by a δ (⁵⁶Fe/⁵⁴Fe) of 1.3‰; This difference may be used to trace the distribution of microorganisms in modern and ancient earth (Beard et al. 1999).

Field observations and laboratory experiments on red soils containing both hematite and goethite have shown that if exposed to anaerobic conditions they turn yellow, a process termed *xanthization*. The colour change is due to preferential reduction of hematite (red) over goethite (yellow). These observations agree with results of Barrón and Torrent (1987), who found a significant correlation between the concentration of Fe oxides in red Spanish soils and their hematite content (Fig. 12.30). After a 512 h laboratory treatment with dithionite red tropical soils turned yellow (Jeanroy et al., 1991). The preferential dissolution of hematite may be a specific property of this mineral, but because Al has a stabilizing effect on the structure it may also be due to the commonly lower Al substitution as compared with that in the coexisting goethite (Torrent et al., 1987) (see Fig. 12.23).

In conclusion, it appears necessary to study more extensively those properties of the various oxides, which determine their specific dissolution behaviour. As pointed out by Postma (1993), the variation in reactivity, a solid phase parameter, may, in some cases, be twice as high as the effect of the type of dissolution (protonation, complexation, reduction).

13

Formation

13.1

General

Although much is known about methods of synthesizing iron oxides (Schwertmann & Cornell, 2000), the details of the mechanisms governing a particular synthesis route are still incompletely understood. In essence, formation involves two basic mechanisms:

- (1) *direct precipitation* from Fe^{II} - or Fe^{III} -containing solutions (described in this chapter) and
- (2) *transformation* of an Fe oxide precursor, either by a dissolution/reprecipitation process or via a solid state transformation involving internal rearrangements within the structure of the solid precursor (described in chapter 14).

A summary of the main pathways by which the Fe oxides form is given here and expanded in this and in chapter 14.

Goethite forms in aqueous media by direct precipitation from soluble Fe^{III} species which are supplied by hydrolysis of Fe^{III} solutions, by dissolution of a solid precursor, or by oxidation/hydrolysis of Fe^{II} salt solutions.

Akaganéite and *schwertmannite* form in acidic solutions by forced hydrolysis of FeCl_3 or FeF_3 and $\text{Fe}_2(\text{SO}_4)_3$ solutions, respectively. For akaganéite a threshold concentration of Cl^- or F^- ions must be present.

Lepidocrocite forms by oxidation of aqueous Fe^{II} solutions via a green rust intermediate, but direct precipitation from low molecular weight Fe^{III} species may also take place.

Ferrihydrite precipitates directly from rapidly hydrolysed Fe^{III} salt solutions. At $\text{pH} > 3$, 2-line ferrihydrite precipitates, whereas at lower pH and temperatures close to 100°C , the 6-line variety forms. Ferrihydrite also forms as a result of oxidation of a Fe^{II} salt solution. A full range of intermediate ferrihydrites may be produced in the Fe^{III} system by varying the rate of hydrolysis, or in the Fe^{II} system, in the presence of low levels of Si (Schwertmann & Cornell, 2000). Two-line ferrihydrite does not transform to 6-line ferrihydrite.

Hematite forms by holding Fe^{III} salt solutions at temperatures close to 100°C ("forced hydrolysis") (Matijevic & Scheiner, 1978), from 2-line ferrihydrite in aqueous media at around pH 7, by high temperature solid-state transformation of var-

ious Fe oxide hydroxides through combined dehydroxylation and/or internal reorganisation, by oxidation of magnetite and by thermal decomposition of Fe salts and chelates.

Magnetite is obtained in aqueous, alkaline systems by precipitation from a mixed $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ solution, by oxidation of Fe^{II} solution via green rust or $\text{Fe}(\text{OH})_2$, or by interaction of Fe^{2+} with ferrihydrite. Another pathway involves high temperature reduction of Fe^{III} oxides (e.g. with H_2). *Maghemite* forms topotactically by wet or dry oxidation of magnetite or by heating lepidocrocite and by thermal decomposition of various organic Fe-salts (cf chap. 20).

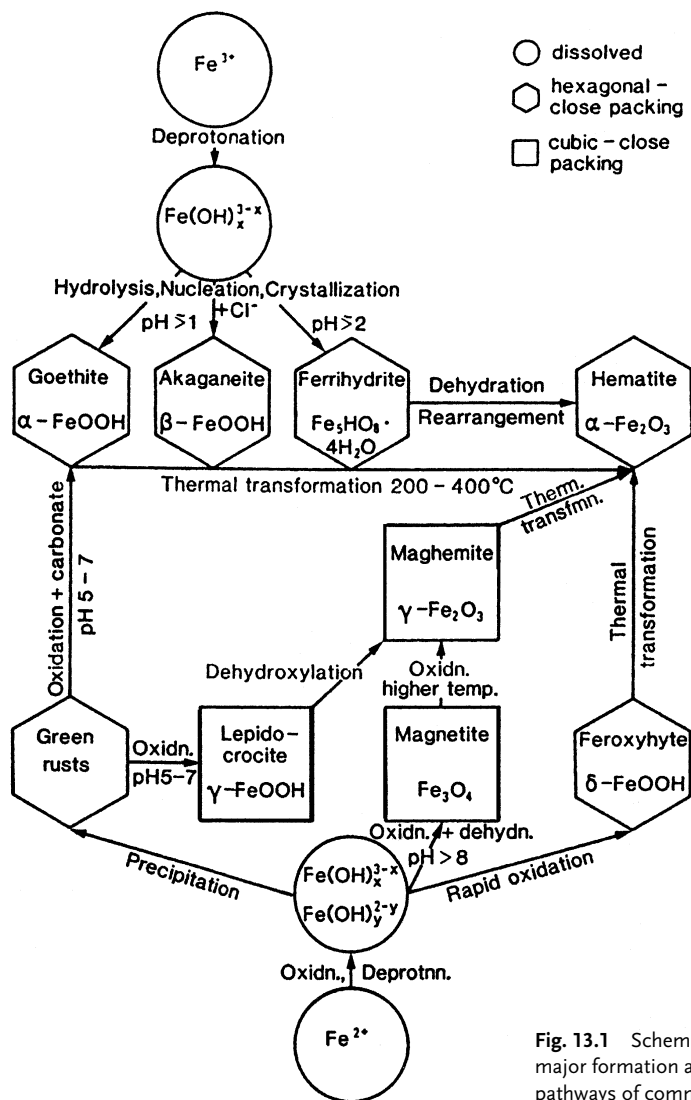


Fig. 13.1 Schematic representation of major formation and transformation pathways of common iron oxides.

From this short overview it follows that iron oxides can form by the following main pathways:

- Hydrolysis of Fe^{III} salt solutions at various temperatures and pHs (OH/Fe-ratios);
- Oxidation of Fe^{II} salt solutions followed by hydrolysis
- Thermal decomposition of metal chelates
- Thermal transformation of solid phases in the dry state or via solution (Chap. 14)
- Dissolution/precipitation reactions.

Various pathways are depicted in Figure 13.1.

The formation of Fe oxides in rocks and in soils is discussed in chapters 15 and 16, respectively, and the role biota play is treated in chapter 17.

13.2

Formation in Fe^{III} systems

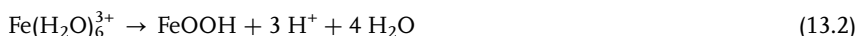
13.2.1

Hydrolysis reactions

In the presence of water, an Fe^{III} salt dissociates to form the purple, hexa-aquo ion, i. e.



The electropositive cation induces the H₂O ligands to act as acids and, except at very low pH, hydrolysis, i. e. deprotonation of these ligands, takes place. The process is step-wise with ultimately all six ligands being deprotonated. The rates of water exchange, $k_{\text{ex}}^{\text{H}_2\text{O}}$, for Fe(H₂O)₆³⁺, FeOH(H₂O)₅²⁺ and Fe(OH)₂(H₂O)₄⁺ were estimated to be 1.6 · 10²; 1.4 · 10⁵ and 10⁶ s⁻¹; respectively (Grant & Jordan, 1981; Schneider & Schwyn, 1987). Complete hydrolysis corresponds to formation of an Fe^{III} oxide or oxide hydroxide, i. e.



Hydrolysis is commonly induced by addition of a base¹⁾, by heating (forced hydrolysis) or by dilution; it can also be induced by solvent extraction or ion exchange (Segal, 1984). Al in the system enhances hydrolysis (Shah Singh & Kodama, 1994). The many investigations of this process have been reviewed by Sylva (1972), Flynn (1984), Schneider and Schwyn (1987), Cornell et al. (1989), Rose et al. (1997) and Schwertmann et al. (1999).

1) A problem with this method of hydrolysis is that addition of a base (especially NaOH) leads to local pH gradients and, hence, variations in the hydrolysed species that form (Schneider, 1984), and so makes reproducible results difficult to obtain. Attempts to minimize this effect have included replacement of NaOH with

weaker bases such as NaHCO₃ and imidazole (Feitknecht and Michaelis, 1962; Schneider, 1984), construction of a special apparatus to achieve homogeneous mixing (Dousma & Bruyn, 1976), and extraction of the acid from the solution with a primary amine (Magini, 1977).

Initially, low molecular weight species form, i.e.



These equilibria are established rapidly. The relevant equilibrium constants are listed in Table 9.2. Above a threshold OH/Fe (ca ~1). The low molecular weight species interact to produce species with a higher nuclearity, e.g. the dimer,



Such reactions become faster as the charge per Fe decreases.

The existence of monomers and dimers at OH/Fe ratios of up to 0.5 in an $\text{Fe}(\text{NO}_3)_3$ solution has been demonstrated by Mössbauer spectroscopy (Fig. 13.2): the monomers produced a broad singlet with an isomer shift of $\delta = 0.38 \text{ mm s}^{-1}$, whereas the dimer showed distinct quadrupole splitting with $\Delta E_Q = 1.20 \text{ mm s}^{-1}$ and $\delta = 0.45 \text{ mm s}^{-1}$. The doublet indicates that the Fe^{III} ion is subjected to a large, uniform electric field gradient arising from some considerable asymmetry in the surrounding coordination sphere. The sharp lines suggest high structural order (Johnston & Lewis, 1986).

The formation of the dimer is rapid with $k_{12} = 630 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, 3 M NaClO_4), whereas breakdown is of the order of seconds; $k_{21} = 0.4 \text{ s}^{-1}$ (Lutz & Wendt, 1970; Po & Sutin, 1971). Consequently, further polymerization may be very rapid. On the other hand, the breakdown of the dimer (and also of higher molecular weight species) is accelerated by protons, i.e.



$$\frac{-d[\text{Fe}_2(\text{OH})_2^{4+}]}{dt} = (k_1 + k_2 [\text{H}^+]) [\text{Fe}_2(\text{OH})_2^{4+}] \quad (13.8)$$

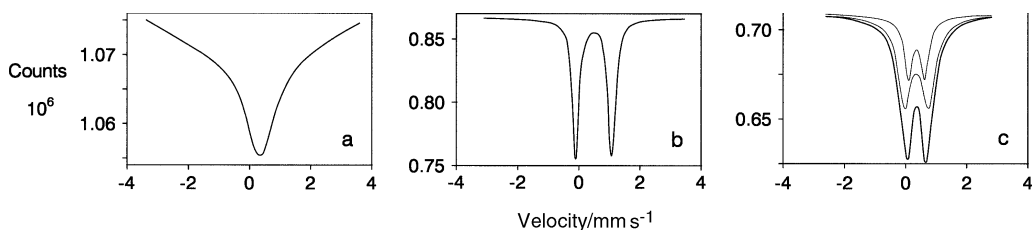


Fig. 13.2 Mössbauer spectra at RT of an $\text{Fe}(\text{NO}_3)_3$ solution (a) unhydrolysed (OH/Fe = 0); (b) hydrolysed at OH/Fe = 0.2 and (c) hydrolysed at $\text{CO}_3^{2-}/\text{Fe} = 0.5$ for 40 h (Johnston & Lewis, 1986, with permission).

where $k_1 = 0.4 \text{ s}^{-1}$ and $k_2 = 3.1 \text{ M}^{-1}\text{s}^{-1}$ (Flynn, 1984). Breakdown becomes increasingly slower as the molecular weight of the hydrolysis species increases.

Trimers (except in chloride solutions) and tetramers have not been identified directly, although a number of authors in the past and again more recently (Daniele et al., 1994) claimed to have identified a trimer on the basis of potentiometric data. Schneider has developed a model for the structural variety of *trimers* that could form from the hydrolysis of dimers in chloride solutions (Schneider & Schwyn, 1987). A general formula $\text{Fe}_3\text{O}_r(\text{OH})_s^{9-(2r+s)}$ has been suggested and includes Fe-OH-Fe (*olation*) as well as Fe-O-Fe (*oxolation*) bridges.

Further hydrolysis leads to a red brown polynuclear compound; whether this is suspended or precipitated depends mainly on the pH and the ionic strength of the system. The nature of the polynuclear species has been the subject of a great number of studies in the past. Many of the earlier studies aimed at characterizing these polynuclears, concentrated on the colloidal properties of the suspensions and used techniques such as photocorrelation spectroscopy, (laser) light scattering, (ultra) centrifugation, gel and membrane filtration, flocculation and sedimentation behaviour, charge properties, kinetics of formation and dissolution, pH relaxation (Feitknecht & Michaelis, 1962; Spiro et al., 1966; Sommer & Margerum, 1970; Hsu & Ragone, 1972; Hsu, 1973; Danesi et al., 1973; Knight & Sylva, 1974; Murphy et al., 1976a, 1976b, 1976c; Ciavatta & Grimaldi, 1975; Dousma & DeBruyn, 1976, 1978; Music et al., 1982; Van der Woude & De Bruyn, 1983; Van der Woude et al., 1983; Segal, 1984; Schneider, 1984; Schneider & Schwyn, 1987; Blesa & Matijevic, 1989 (review)).

However, as methods such as XRD and ED, HRTEM, EXAFS, XPS and MS (see chapter 7), for long- and short-range solid-state analysis, were developed, more direct information especially about the nano-sized polymers was obtained (Atkinson et al., 1968, Murphy et al., 1975, 1975a, Johnston & Lewis, 1986, Lewis & Cardile, 1989; Khoe & Robins, 1989; Bottero et al., 1991;1994, Tchoubar et al., 1991; Rose et al. 1997; Doelsch et al. 2000). Johnston and Lewis (1986) separated the species in partly neutralized 0.1 M $\text{Fe}(\text{NO}_3)_3$ solutions into different molecular weight fractions by ultrafiltration (Amicon Diafilters) and examined each fraction with Mössbauer spectroscopy. In all fractions Fe^{III} was octahedrally coordinated. Monomers and dimers predominated in the <500 fraction when no base was added. As OH/Fe increased to 0.5, the proportion of polymer species (MW >500) increased from 12 to 44% and at OH/Fe = 2.0, the polymer size increased, with 80% being in the 50k–300k fraction (Tab. 13.1). All these polymers invariably displayed a broad doublet which could be fitted to two closely overlapping Fe^{III} doublets with quadrupole splittings at RT of

Tab. 13.1 Distribution of molecular weight (MW) fractions in an $\text{Fe}(\text{NO}_3)_3$ solution of OH/Fe = 2.0 after 4 days (Johnston & Lewis, 1986; with permission).

Nominal MW range of fraction	>300k	100–300k	50–100k	20–50k	10–20k	1–10k	<1k
% of total	311	5	41	3	0.3	2	18

0.51 and 0.85 mm s⁻¹, respectively, i.e. slightly larger than the parameters for ferrihydrite (0.50 and 0.83 mm s⁻¹). The two doublets are considered to represent the extremes of a continuum of doublets arising from the slightly differing site geometries in this poorly ordered polymeric material. From these results, the authors concluded that dimers are the most probable building units for formation of polymers; this is in line with the proposal of Knight and Sylva (1974).

This also agrees, in principle, with the EXAFS work of Rose et al. (1997), who reported “chaotic” polymerization of the dimers, leading to a solid phase which was most probably 2-line ferrihydrite. Combes et al. (1989) used XANES and EXAFS to examine the short range ordering of polynuclears formed in 0.1 M and M FeCl₃ and Fe(NO₃)₃ solutions at OH/Fe ratios of up to 2.8. The monomeric, Cl⁻ containing, aquo complexes (i.e. Fe(OH₂)₄ Cl₂⁺) found at OH/Fe = 1.0 formed polynuclears at OH/Fe > 1.0, with Fe-Fe distances of 0.305 and 0.344 nm which were assigned to edge and corner contact between two octahedra, respectively (see Chap. 2). The number of these contacts increased with increasing degree of hydrolysis; this was considered to indicate increasing particle size although as EXAFS only reflects *local* ordering, it could not be proven.

13.2.2

Formation of the different Fe^{III} oxides

The formation of solid Fe oxides in the Fe^{III} system requires the hydrolysis of the Fe^{III}-hexa aquo cation Fe^{III}(OH₂)₆³⁺ as described in the previous section. All the different Fe^{III} oxides may form by growth of nuclei fed by low-molecular weight species. The key factor which governs the oxide that forms and its crystallinity is the rate at which these species, mainly the monomers and dimers, are supplied to the growing crystal. The more slowly the hydrolysed species are supplied, the better ordered are the phases that result. The directing factors in this polymerization/crystallization process are pH, [Fe^{III}] and temperature. In general, ferrihydrite is favoured when the rate of supply of growth units is relatively rapid, whereas a slow rate of supply leads to more crystalline oxides, such as goethite and hematite. As seen from the XRD patterns (Fig. 13.3), a full range of ferrihydrites with between 2 and 6 lines on the one hand and goethite/lepidocrocite on the other, can be obtained by varying the rate of hydrolysis in a pure Fe^{III}-system at RT and pH 7 from between 0.13 and 66 μmol OH/mmolFe per min (Fig. 13.3, left) (Schwertmann et al. 1999). A common way of producing a 6-line ferrihydrite, suggested by Towe & Bradley (1967), is by dialysing a Fe^{III}nitrate solution against distilled water at RT after 12 min of hydrolysis at 85 °C. A precursor of this 6-line ferrihydrite has been identified in a sol that was freeze-dried before dialysis. XRD showed that this phase has a tunnel structure analogous to that of akaganéite and schwertmannite with nitrate (10 wt%) probably being located in the tunnels (Schwertmann et al. 1996). The bulk composition after drying at 110 °C was FeO(OH)_{0.8}(NO₃)_{0.2}. This material decomposed to 6-line ferrihydrite upon further hydrolysis at RT. Ferrihydrite has also been identified in nature as a slow hydrolysis product of scorodite (FeAsO₄ · 2 H₂O) (Walenta, 1982).

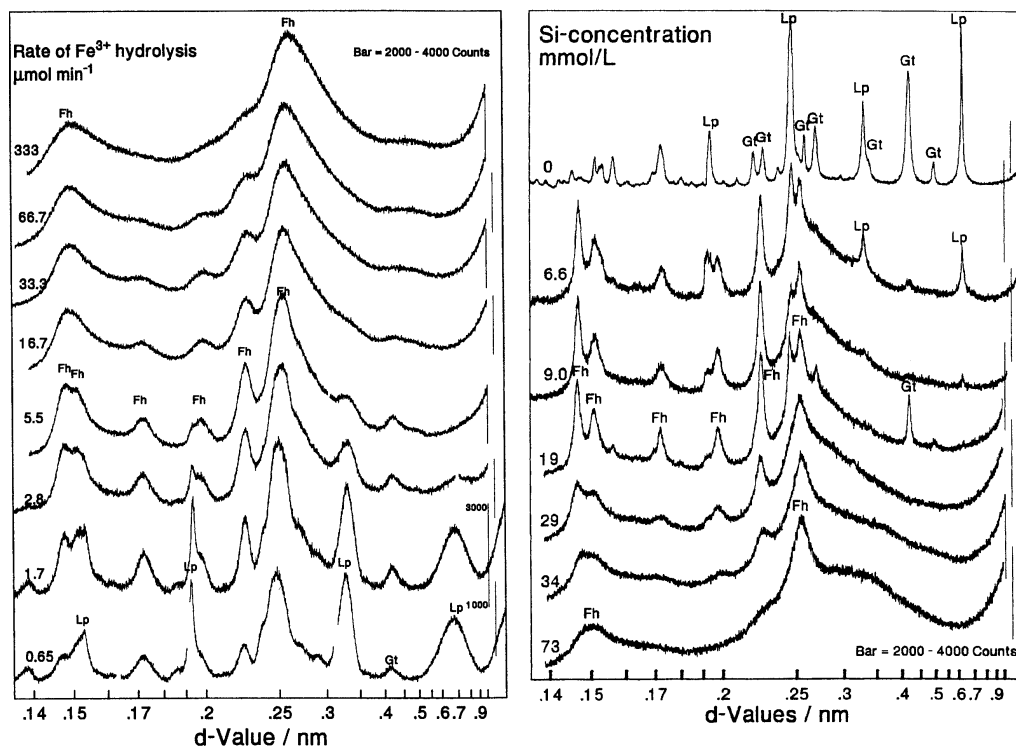


Fig. 13.3 X-ray diffractograms of Fe oxides produced at RT by hydrolysing a 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution at a different rates (left) and by oxidizing a 0.1M FeCl_2 solution at pH 7 in the presence of various Si concentrations (right); Fh: ferrihydrite; Gt: goethite; Lp: lepidocrocite. (Schwertmann et al.1999; with permission; Schwertmann & Cornell 2000).

As indicated above, the hydrolysis of an Fe^{III} salt solution may also lead directly to goethite, lepidocrocite, akaganéite and hematite – or mixtures of these compounds depending on the experimental conditions. This occurs when the supply rate of growth units is such that the solubility products of these oxides, but not the much higher one of ferrihydrite, are exceeded. Such a situation arises at very low pH ($\text{OH}/\text{Fe} < 1$) or, at higher OH/Fe , if the growth units are supplied so slowly that the spatial ordering leading to better crystals can be achieved (Knight & Sylva, 1974; Schneider, 1984; Schwertmann et al. 1999). The better crystalline Fe oxides also form over a wide pH range by transformation of ferrihydrite; the mechanisms involved are discussed in chapter 14. The time required for crystallization, which ranges from minutes to years, and also the oxide formed, depend on such factors as temperature, OH/Fe , $[\text{Fe}^{3+}]$ and the nature of the anion. Seeding and the presence of additives can have a directing effect on the product. Formation of the different oxides in acid media is discussed in the following section.

Hematite is promoted by high temperatures ($>70^{\circ}\text{C}$), by high $[\text{Fe}]$ and, at high temperatures, by addition of acid to lower the pH (Robins, 1967; Hsu & Wang, 1980). Under hydrothermal conditions (150°C) formation of hematite is very rapid (Riveros & Dutrizac, 1997). In chloride containing systems akaganéite occur as an intermediate phase. The so-called “monodispersed”, i.e. uniform, hematite crystals produced by the “sol-gel” method at temperatures close to 100°C (see chap. 4) are preceded by akaganéite as an intermediate phase (Sugimoto, 2001). It is essential that the Fe salt is added to preheated water rather than to water at room temperature in order to avoid nucleation of goethite during the initial heating stage. Van der Woude et al. (1983) found that seeding with hematite promoted additional hematite formation in acid media and that at $\text{pH} < 1$ and temperatures greater than 80°C , hematite and ferrihydrite appeared to form competitively; the activation energies for nucleation and growth of hematite were 47 ± 4 and $50 \pm 5 \text{ kJ mol}^{-1}$, respectively. Riveros & Dutrizac (1997) found that seeding with hematite accelerated precipitation and increased the filterability of the product.

Goethite is the sole FeOOH polymorph that forms directly from $\text{Fe}(\text{NO}_3)_3$ solutions at zero and low additions of base, whereas both goethite and lepidocrocite formed from $\text{Fe}(\text{ClO}_4)_3$ solutions (Feitknecht & Michaelis, 1962; Fordham, 1970; Hsu, 1973; Knight & Sylva, 1974; Murphy et al., 1975; 1976). In $\text{Fe}(\text{ClO}_4)_3$ solutions to which no base had been added, goethite predominated at temperatures up to 37°C , but was replaced by hematite at temperatures above 55°C (Wang & Hsu, 1980). Acicular goethite crystals, ca. 20nm long and 5nm wide, bounded by (101) and (210) faces and associated in rafts (see Fig. 4.7) form from a partially neutralized Fe^{III} nitrate solution at $\text{pH } 1.6\text{--}1.8$ at 25°C after 60 days (Morup, 1983; Glasauer et al. 1999) whereas at 70°C separate, larger crystals result after 24 hr (Cornell, unpubl.).

Akaganéite requires the presence of chloride or fluoride ions (Bernal et al., 1959). The strong akaganéite-directing effect of chloride is shown by the fact that even in boiling FeCl_3 solutions, akaganéite forms initially in preference to hematite. Seeding an FeCl_3 solution with goethite before the start of hydrolysis promotes considerable goethite formation, but has no effect if the solution is partly hydrolysed. This indicates that the chloride ion participates from the earliest stage of the reaction (Atkinson et al., 1977). Correspondingly, addition of chloride ions to Fe nitrate solutions, once hydrolysis has started, does not promote formation of akaganéite. Hematite forms competitively with akaganéite at reaction temperatures above 90°C (Atkinson et al. 1977). Riveros & Dutrizac (1997) found that if sufficient hematite seeds were added, hematite formed in preference to akaganéite, even at 60°C .

Upon hydrolysis of an FeCl_3 solution at $\text{OH}/\text{Fe} = 1.5$, dimers consisting of two edge sharing octahedra form first, followed after 50 min by trimers with additional corner sharing; these then condense to an Fe_{24} -polycation which has the akaganéite structure (Bottero et al. 1994). These observations are in line with earlier suggestions that the trimer forms the basic structural unit, termed the structural embryo, of akaganéite (Fig. 13.4). This embryo has a stoichiometric composition of $\text{Fe}_3\text{O}_2(\text{OH})_2\text{Cl}$ (Schneider 1984, 1988; Schneider & Schwyn, 1987) and its formation is directed by the chloride ion which tracer studies (Jiskra, 1983) have shown to be associated with the embryo in a position of minimum energy by an outer sphere linkage. Schneider

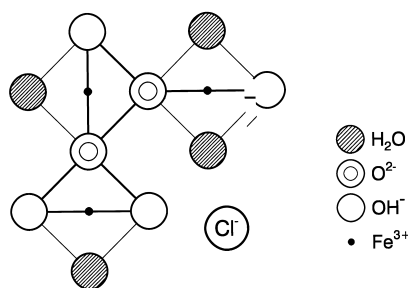


Fig. 13.4 The structural “embryo” of akaganéite (Schneider & Schwyn, 1987, with permission).

and his coworkers used laser light scattering, Mössbauer spectroscopy, magnetic susceptibility and XRD to show that the polymers transformed to akaganéite by a dissolution/reprecipitation process during which the shape of the polynuclear arrays changed, whereas the internal akaganéite structure was maintained. The polynuclear arrays became wider as FeOH^{2+} species released from the ends of the arrays by acid cleavage were redeposited at the centers. The kinetics of this process was governed by the dissolution step.

Like the chloride ion, the sulphate ion appears to have a structure-building effect in acid media, i.e. when the extent of hydrolysis is low. The effect depends on both $[\text{SO}_4^{2-}]$ and pH. At high $[\text{SO}_4^{2-}]$ and in the presence of monovalent cations, especially K^+ , hydrolysis of Fe^{3+} leads to the formation of Fe^{III} -hydroxy-sulphates, the so-called *jarosites* – $\text{MFe}_3(\text{OH})_6(\text{SO}_4)_2$ – where M can be Na^+ , K^+ , NH_4^+ or H_3O^+ (Haigh, 1967; Matijevic & Scheiner, 1978; Sapieszko & Matijevic, 1980; Music et al., 1982; 1993). Dousma et al. (1979) suggested that SO_4^{2-} inhibits the oxolation process and Thompson and Tahir (1991) found that an $\text{SO}_4^{2-}/\text{Fe}^{3+}$ ratio > 1 induced formation of stable Fe^{III} sulphate complexes and thus increased the pH required for the onset of precipitation of iron oxides. In the presence of sulphate ($\text{SO}_4/\text{Fe} = 0.3$), forced hydrolysis of FeCl_3 solution gives almost 100% goethite (Sugimoto & Wang, 1998).

At somewhat higher pH (2 to 4) *schwertmannite*, an Fe^{III} oxy-hydroxy sulphate $\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y$, forms in the sulphate system: it is analogous to akaganéite in the chloride system (Brady et al., 1986; Bigham et al., 1990; Bigham & Nordstrom, 2001). Schwertmannite can be synthesized by a brief (12 min) forced hydrolysis at 60°C of a mixed 0.02 M FeCl_3 /0.01 M NaSO_4 solution. A phase with a structure analogous to that of schwertmannite also forms if selenate (Waychunas et al. 1994) or chromate (Regenspurg, pers. com. 2001) replace sulphate. If arsenate competes with sulphate, schwertmannite is formed up to an $\text{As}/(\text{As}+\text{S})$ mole ratio of ca. 0.4, a poorly ordered Fe^{III} hydroxy arsenate at a ratio of ca 0.8 and a mixture of the two phases in between these two ratios (Carlson et al. 2002; Regenspurg, pers. com. 2001).

Where *lepidocrocite* forms from Fe^{III} salt solutions it is often associated with goethite. It has been observed in partially hydrolysed Fe^{III} nitrate solutions at low pH (Murphy et al. 1976c) (Fig. 13.5) and during very slow hydrolysis at pH 7 (see Fig. 13.3) (Schwertmann & Cornell, 2000) suggesting that it can form directly from low concentrations of low-molecular weight precursors.

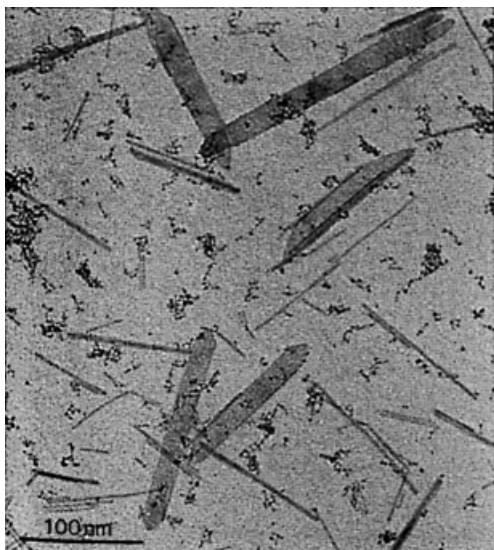


Fig. 13.5 Lepidocrocite (laths), goethite (needles) and ferrihydrite (spheres) formed after 750 d in a 0.018 M $\text{Fe}(\text{ClO}_4)_4$ solution with $\text{OH}/\text{Fe} = 1.88$ at RT (Murphy et al. 1976b, with permission; courtesy A. Posner).

Additives may affect the purity of the phases formed. The product resulting from the refluxing of a FeCl_3 solution at 100°C was modified by addition of various organic additives ($\text{A}/\text{Fe} = 0.2$) (Reeves & Mann, 1991). Generally ca. 90% of the product was in the form of a red sol which could not be isolated. In the presence of chloride, sulphate, phosphate and perchlorate and also organic phosphates, phosphonates and diphosphonates, the 10% better crystallized material was hematite. Most of the other organic additives (methyl-dihydrogen phosphate, naphthyl-disodium orthophosphate and methyl and phenyl phosphonic acid) induced lepidocrocite formation, but 1–2 ethylene diphosphate promoted akaganéite. The authors attempted to explain these effects in terms of the partial charge model (Livage et al., 1988); they calculated the partial charge of water in the Fe^{III} complexes $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_2\text{X}]^0$ and found that this could be correlated with the electronegativity of the additive and the tendency to favor olation or oxolation. The less electronegative additives (negative partial charge) favoured olation and hence FeOOH even at high temperatures. At present there is no explanation of why akaganéite formed; it should be noted, however, that another organic molecule, dihydroxy-ethylene glycol, has been reported to induce formation of well crystalline akaganéite (Nightingale & Benck, 1960). Mixed solvents – water/ethanol or water/ethylene glycol promoted fast precipitation of akaganéite from heated FeCl_3 solutions (Hamada & Matijevic, 1982; Matijevic & Cimas, 1987). These mixed solvents enhanced hydrolysis of Fe^{3+} and promoted formation of iron chloride complexes. If Si is present ($\text{Si}/\text{Fe} 0.3$) akaganéite formation is suppressed (Cornell, 1992). EXAFS data showed that as the Si concentration increased from Si/Fe of 0 to 4 mol mol^{-1} , three-dimensional polymerization of an aqueous FeCl_3 solution to akaganéite at low Si concentration changes into two-dimensional polymerization and more and more X-ray amor-

phous material is formed; polymerization is at a minimum at Si/Fe = 1 (Doelsch et al. 2000). Urotropin (hexamethylenetetramine) also hinders akaganéite formation at 90 °C (Saric et al. 1998). High levels of citrate and phosphate inhibit hydrolysis of Fe^{III} solutions via complexation of Fe^{III} (Spiro et al., 1966; Van der Woude et al., 1986; Kandori et al., 1992).

13.3

Formation in aqueous Fe^{II} systems

13.3.1

General

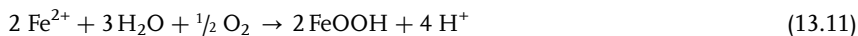
Goethite, lepidocrocite and akaganéite, magnetite, maghemite, ferrihydrite, feroxyhyte and hematite can all be produced from Fe^{II} solutions by oxidation followed by hydrolysis. These processes are of particular interest to the hydrometallurgical industry where efforts are being made to produce pure, high quality iron oxide pigments from Fe oxide byproducts (Chen & Cabri, 1986; Agatzini et al., 1986; Ward et al., 1990; Dutrizac, 1996). Which oxide forms is governed by the pH, the rate of oxidation, the temperature, [Fe²⁺] and also by foreign compounds in the system (Tab. 13.2). Unless the reaction conditions are carefully controlled, mixtures, rather than a monophase product result. A characteristic of this system is the formation of pairs of products, e.g. goethite/lepidocrocite.

Oxidation of Fe^{II} salt solutions has been investigated intensively (Stumm & Lee, 1961; Ghosh, 1976; Tamura et al., 1976; Sung & Morgan, 1980; Davidson & Seed, 1983; Roekens & Van Grieken, 1983; Millero et al., 1987; von Gunten & Schneider,

Tab. 13.2 Conditions for the predominance of one compound in various pairs of oxides formed via oxidation of Fe^{II} salts at pH 4–9

<i>Goethite</i>	<i>Lepidocrocite</i>
CO ₂ present	CO ₂ absent
Sulphate	Chloride
Fast oxidation	Slow oxidation
Lower pH	Higher pH
Al, Mn, Co	–
<i>Lepidocrocite</i>	<i>Ferrihydrite</i>
Slow oxidation	Fast oxidation
pH > 5	pH < 5
<i>Lepidocrocite</i>	<i>Magnetite</i>
Fast oxidation	Slow oxidation
Low temperature	High temperature
Lower pH	Higher pH
Chloride	–
Low [Fe ²⁺]	High [Fe ²⁺]

1991; Vracar & Cerovic, 1997; Rose & Waite, 2002). The oxidation reaction of Fe^{2+} with oxygen¹⁾ can be written as,



In the neutral pH region, the rate of aerial oxidation of Fe^{2+} with oxygen is first order with respect to $[\text{Fe}^{2+}]$ and dissolved oxygen and second order with respect to pH (Stumm & Lee, 1961), i.e.

$$\frac{-d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}] \cdot P_{\text{O}_2} \cdot [\text{OH}^-]^2 \quad (13.12)$$

At 20.5 °C and between pH 6.0 and 7.5, k ranges from $1.28\text{--}1.83 \cdot 10^{-12} \text{ min}^{-1} \text{ MPa}^{-1} \text{ L}^2 \text{ M}^{-2}$. As the above equation indicates, the rate of oxidation increases one hundredfold per pH unit. In other words, oxidation is extremely slow below pH 6 and rises sharply above this value. It also increases tenfold for a 15 °C increase in temperature. Increasing the ionic strength of the system retards oxidation (Sung & Morgan, 1980; Millero et al., 1987). The oxidation/hydrolysis process is accelerated by increasing the stirrer speed (Perez et al. 1998; Perez & Umitu 2000).

Oxidation is accelerated by anions such as F^- , H_2PO_4^- and HPO_4^{2-} and lowered by others in the order, $\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{H}_3\text{SiO}_4^- > \text{Br}^- > \text{I}^- > \text{SO}_4^{2-}$ (Tamura et al., 1976). Small amounts of Cu, Mn, Co and anions which complex Fe^{III} have a catalytic accelerating effect (Stumm & Lee, 1961), whereas organic ligands, particularly those found in natural waters, may retard oxidation (Stumm & Singer, 1966). At pH's above 7, oxidation of Fe^{2+} is autocatalytic, i.e. the reaction is accelerated by the ferrihydrite formed, probably after some Fe^{2+} has adsorbed on the surface (Tamura et al., 1976). Other iron oxides also promote oxidation in the order ferrihydrite < goethite < lepidocrocite < akaganéite (Tamura et al., 1980).

The oxidation and hydrolysis of Fe^{2+} leads to Fe^{III} oxides either directly or via soluble green rust complexes, solid green rusts or $\text{Fe}(\text{OH})_2$. The latter convert to the oxides either by a solid state reaction or a via solution (reconstructive) transformation. Generally, where there is a difference between the structure of the precursor and that of the final oxide, a via solution process seems more likely, but internal rearrangement during topochemical oxidation to the new phase, may also take place.

13.3.2

Effect of pH

In moderately alkaline solutions (pH > 8) oxidation of Fe^{II} solutions proceeds via $\text{Fe}(\text{OH})_2$ and usually yields *magnetite* (David & Welch, 1956; Sidhu et al., 1977). Under these conditions the solubility product of magnetite is exceeded so the mixed oxide is more stable than the pure Fe^{III} oxides (see Chap. 8). Tamaura et al. (1981) monitored the transformation of $\text{Fe}(\text{OH})_2$ at pH 11 and 65 °C. Initially both goethite

1) Formation of Fe oxides most commonly involves oxidation with air or oxygen, but other ox-

dants (KNO_3 , H_2O_2 (violent) or hydroxylamine have also been used.

The formation of intermediate greenish-blue, mixed $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ -phases, so called *green rusts*, predominates if oxidation takes place under *weakly acid to weakly alkaline* conditions because the solubility product of $\text{Fe}(\text{OH})_2$ is then no longer exceeded. At slightly lower pH, the soluble analogues – $\text{Fe}_2^{\text{II}}\text{Fe}^{\text{III}}\text{O}_x(\text{OH})_y^{(7-2x-y)+}$ and $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{O}_x(\text{OH})_y^{(5-2x-y)+}$ – are formed (Misawa et al., 1973, 1973 a, 1974). The solid green rusts are double layer hydroxide salts in which positively charged octahedral Fe hydroxy layers are linked by interlayer anions (Cl^- , SO_4^{2-} , CO_3^{2-}) (see Chap. 2). They are stable only at low redox potential. They form either by direct precipitation from an Fe^{II} salt solution upon oxidation once their solubility product is exceeded (eqn. 13.13), or by interaction between 2-line ferrihydrite precipitated initially and Fe^{2+} in solution (eqn. 13.14); in the presence of a sufficiently high $[\text{Fe}^{2+}]$, the green rust is more stable than 2-line ferrihydrite

$$3 \text{ FeSO}_4 + 0.25 \text{ O}_2 + 4.5 \text{ H}_2\text{O} \Rightarrow \text{Fe}_2^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_5\text{SO}_4 + 2 \text{ H}_2\text{SO}_4 \quad (13.13)$$

$$\text{Fe}_5^{\text{III}}\text{HO}_8 + 10 \text{ FeSO}_4 + 17 \text{ H}_2\text{O} \Rightarrow 5 \text{ Fe}_2^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_5\text{SO}_4 + 5 \text{ H}_2\text{SO}_4 \quad (13.14)$$

(Ferrihydrite) (Sulphate-green rust)

TEM observations have confirmed that large hexagonal plates of green rust form at the expense of ferrihydrite (Mann et al., 1989). The reaction is accompanied by production of an equivalent amount of protons (shown by the consumption of alkali to maintain conditions around neutral) and the loss of Fe^{2+} and the respective anion (Cl^- , SO_4^{2-}) from solution (Fig. 13.6). For the reaction to proceed it is essential that the acid produced during the process is continuously neutralized and that a pH close to neutral is maintained (see the base consumption in Figure 13.6). In the Cl-system, Lewis (1997) observed a fairly constant $[\text{Fe}^{2+}]$ during much of the reaction and a

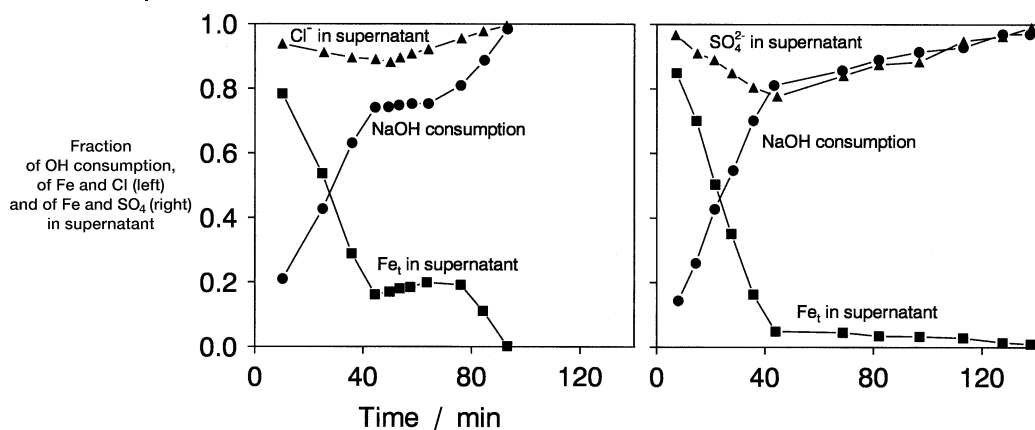
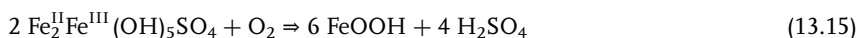


Fig. 13.6 Fraction of OH consumption and of Fe and Cl⁻ (right) and SO₄²⁻ (left) in supernatant during the aerial oxidation of sulfate (right) and chloride (left) green rust at RT (Schwertmann & Fechter, 1994, with permission).

lower reaction rate in the sulphate system; he considered these observation to indicate that there is a critical [Fe²⁺] above which the green rust is stable. Once the [Fe²⁺] falls below the critical level, further oxidation leads to the decomposition of green rust and to the formation of goethite and/or lepidocrocite.



This process has been studied in some detail¹⁾ by Feitknecht and Keller (1950), Derie and Ghodsi (1972), Detournay et al. (1974, 1975, 1976), Solcova et al. (1981), Taylor (1984), Vins et al. (1987), Schwertmann and Wolska (1990), Schwertmann and Fechter (1994), Lewis, (1997) and Bernali et al. (2001). The structural differences between the educt and product (sheets vs. double bands of octahedra) suggest a via solution transformation. At slightly lower pH, goethite and lepidocrocite form from soluble green rust complexes, possibly because the solubility product of solid green rust is no longer exceeded.

At elevated temperatures (85 °C), oxidation of FeSO₄ solution at pH 4.0–7.5 with hydroxylamine sulphate led to hematite in acid media, to goethite at around pH 6 and to magnetite above pH 7 (Ardizzone & Formaro, 1985). A variation of this procedure is used industrially in the production of goethite as a precursor of maghemite for magnetic tapes. Whereas the initially formed platelets of green rust make the suspension thixotropic, the acicular goethite into which they are converted causes rheopectic behaviour.

1) In these experiments, two main approaches have been followed: either a constant pH has been maintained by addition of base or, alter-

natively, the pH has been allowed to fall as the reaction proceeded.

In *acid media*, green rust phases do not form. The Fe oxides precipitate directly from soluble Fe^{III} and are no longer linked to the initial [Fe²⁺]. At pH < 5 and at RT, ferrihydrite forms (Schwertmann & Thalmann, 1976). In the pH range 2.5 to 4 oxidation is kinetically hindered; this can be assisted by chemo-autotrophic bacteria such as *Thiobacillus ferrooxidans*. Oxidation leads to jarosite (if K is present), schwertmannite, and ferrihydrite/goethite (Bigham et al., 1990; Stahl et al., 1993). An example is presented in plate 13.I: where Fe²⁺-containing acid mine water of pH 3.7 is neutralized to pH 8.2 by carbonate rock, schwertmannite formation is replaced by the formation of 2-line ferrihydrite (E. Murad, unpubl.). At pH 2 and 70 °C, FeCl₂ solution is oxidized to akaganéite (Kiyama & Takada, 1972). The oxidation products of Fe^{III} bromide solution depended on the temperature; as this increased from 10 °C to 80 °C, first akaganéite, then lepidocrocite and goethite and finally hematite formed (Kiyama & Takada, 1972). A range of Fe^{III} oxides also precipitated when Fe^{II} sulphate solution was oxidized in the presence of metallic iron at 50–80 °C (Kiyama et al. 1972). An adaptation of this method is used in the industrial production of pigments.

13.3.3

Effect of oxidation rate

The rate of oxidation depends on the pH and temperature of the system, O₂ solubility (which falls with rising temperature), type and speed of agitation and the geometry of the reaction vessel. All these factors have to be taken into account, particularly in the pigments industry where production of a pure product is as much a matter of engineering design as chemistry. The oxidation rate can be controlled by adjusting the rate of air or oxygen flow into the system.

Under otherwise similar conditions, low oxidation rates appear to promote magnetite and goethite, whereas high rates favor lepidocrocite. Magnetite formation probably requires slow oxidation because complete dehydroxylation of the precursor (green rust) prior to complete oxidation is only possible if sufficient time is available; if, on the other hand, complete oxidation is fast and precedes dehydroxylation, lepidocrocite forms in preference to magnetite (Schwertmann & Taylor, 1977). Dehydroxylation and oxidation appear to be competing reaction steps.

Feroxyhyte (δ' -FeOOH) and δ -FeOOH form over a wide pH range if the rate of oxidation is extremely high – as a result of addition of H₂O₂ or exposure of Fe(OH)₂ to air (Glemser & Gwinner, 1939; Feitknecht, 1959; Feitknecht et al., 1969; Misawa et al., 1974; Carlson & Schwertmann, 1980). At pH 12, well crystallized δ -FeOOH forms, but as the pH drops, the product becomes increasingly less ordered leading to feroxyhyte (Feitknecht, 1959; Carlson & Schwertmann, 1980). The rapid transformation of Fe(OH)₂ when oxidized by H₂O₂ at pH 12, is probably a solid state process, as both Fe(OH)₂ and δ -FeOOH have the CdI₂ structure and conversion between two hcp anion frameworks is relatively easy (Feitknecht, 1959). The overall result is that the Fe^{II} ions in alternate octahedra along the *c*-axis are oxidized and then rearrange in a random manner over the octahedral sites. δ -FeOOH has exactly the same morphology as its precursor which further supports the concept of a topotactic transformation.

13.3.4

Effect of foreign compounds

As with most other Fe oxides, the phases formed by oxidation of green rusts or $\text{Fe}(\text{OH})_2$ are influenced by foreign compounds in the system. A particularly strong effect was found with the various anions. *Chloride* and other halogenides promote lepidocrocite (Detournay et al., 1976; Taylor, 1984). It has been suggested that Cl^- retards magnetite formation by hindering the condensation of neighbouring OH groups to form Fe-O-Fe linkages. *Sulphate* had a goethite promoting effect. Whereas the oxidation of $\text{Fe}(\text{OH})_2$ at $[\text{SO}_4] = 0.03 \text{ M}$ and pH 11 leads to magnetite, only goethite is formed at $[\text{SO}_4] = 0.1 \text{ M}$ (Tamaura et al., 1981).

The effect of *carbonate* has been investigated by oxidizing green rust with a gas mixture containing varying proportions of O_2 and CO_2 . Mixtures of goethite and lepidocrocite formed with the proportion of goethite rising as the CO_2/O_2 ratio increased (Fig. 13.7) (Schwertmann, 1959a; Fey & Dixon, 1981; Carlson & Schwertmann, 1990). The presence of IR adsorption bands at 1300 and 1500 cm^{-1} indicate that the goethite always contains some perturbed and tightly bound carbonate anions. This anion may direct the spatial arrangement of the double chains of $[\text{FeO}_3(\text{OH})_3]$ octahedra common to both FeOOH forms (see Chap. 2). Alternatively, TEM observations have suggested that carbonate ions may suppress nucleation of lepidocrocite (Cornell et al., 1989a). Phosphate suppressed the goethite-favouring effect of carbonate (Torrent and Barron, 2000). To simulate Fe oxide formation in a natural calcareous environment, Loeppert et al. (1984) and Loeppert and Hossner (1984) oxidized Fe^{2+} solutions in the presence of solid CaCO_3 (calcite). The latter neutralizes the protons arising from hydrolysis of Fe^{III} , i.e.

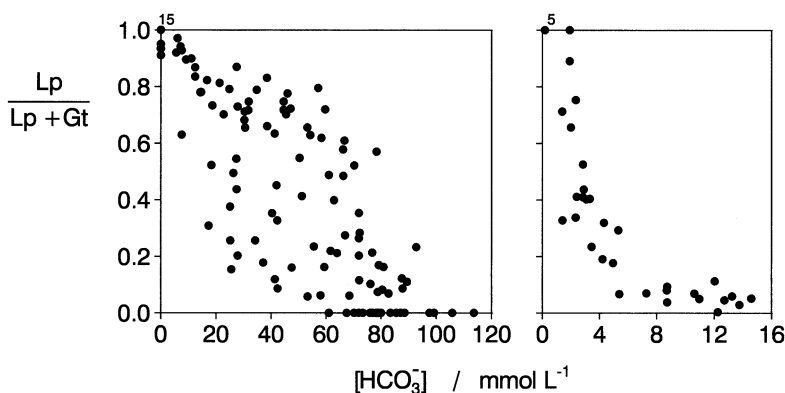


Fig. 13.7 Ratio of lepidocrocite to goethite ($\text{Lp}/(\text{Gt}+\text{Lp})$) produced by oxidation of a FeCl_2 solution at RT and pH 7 (left) and pH 6 (right) as a function of $[\text{HCO}_3^-]$ in the solution (Carlson & Schwertmann, 1990, with permission).

Goethite only formed if CO₂ were present. Oxidation with air alone produced lepidocrocite, the crystallinity of which was much higher with slow oxidation (static system, low P_{O₂}) (Clarke et al., 1985). The failure of CaCO₃ to induce goethite formation despite the presence of carbonate, is probably due to the low solubility of CaCO₃ and/or the coating of its surface by both oxides (Fig. 13.8). Goethite and some lepidocrocite also resulted from oxidation of synthetic siderite (FeCO₃); a via solution process was involved (Schwertmann, unpubl.). In considering the effect of the anion on the product, it must be kept in mind that the stability of the green rust precursor depends on the interlayer cation and increases in the order Cl⁻ < SO₄²⁻ < CO₃²⁻ (Taylor & McKenzie, 1980); this, in turn, may influence the oxidation rate and thereby, the end product.

Silicate hinders formation of lepidocrocite, most probably by blocking nucleation; ferrihydrite forms instead (Schwertmann & Thalmann, 1976; Karim, 1984; Golden & Dixon, 1985). Upon oxidation of simulated groundwaters containing 3–20 mg/L Fe²⁺ and 12 mg/L Si, lepidocrocite formed below an Si/Fe of 0.4, but at higher ratios, only ferrihydrite precipitated (Schwertmann et al., 1984). If silicate is constantly added during the oxidation of a 0.1M FeCl₂ solution together with the NaOH needed to maintain a constant pH (pH 7), increasing Si concentration from zero to 73 mmol/L leads to a full range of oxides from lepidocrocite/goethite at low [Si], to 6-line ferrihydrite at medium [Si] of 5–10 mmol/L and to 2-line ferrihydrite at ca. 70 mmol/L (Fig. 13.3, right) (Schwertmann & Cornell, 2000). Krause and Borowska (1963) reported that AsO₄³⁻, MoO₄²⁻ and WO₄²⁻ promoted goethite over lepidocrocite.

Citrate and phosphate also suppressed the formation of FeOOH polymorphs (Detournay et al., 1975) and phosphate that of magnetite (Tamura et al. 1979; Mann et al., 1989). During oxidation of a carbonate containing FeSO₄ solution at pH 5.5, 7.0 and 8.5, phosphate (P/Fe of up to 0.20) suppressed goethite in favor of lepidocrocite, i. e. phosphate eliminated the goethite-favouring effect of carbonate, probably by replacing carbonate as an adsorbed species. The crystallinity of the lepidocrocite decreased with increasing P/Fe ratio and most of the retained phosphate was not NaOH extractable and therefore considered to be occluded (Cumplido et al. 2000). At pH 6, citrate (citrate/Fe = 0.1) retarded the oxidation of Fe²⁺ in a perchlorate solution and shifted the product from goethite to lepidocrocite at low citrate/Fe ratios and to ferrihydrite at higher ones (Krishnamurti and Huang, 1991; Lui & Huang, 1999). *Sucrose* suppressed the formation of magnetite at temperatures ≤ 40 °C (Tamura et al. 1979).

Of the *cations*, more than 5 mol mol⁻¹ Mn or Co favoured lepidocrocite over goethite (Detournay et al., 1975). Inouye et al. (1971) reported that up to 0.03 Cu strongly promoted magnetite from Fe(OH)₂, but at higher levels had a suppressing effect, whereas Ishikawa et al. (1999) found that magnetite formed at 0.10 mol/mol Cu and goethite at 0.30 mol/mol. Andreeva et al. (1991), and Tabakova et al. (1992) noted that Mn²⁺ catalysed formation of goethite from Fe^{II} sulphate at pH 4.5. Cations inhibited lepidocrocite formation in the order Mo > Cu > Co > Ni > Zn > Mn (Karim, 1984a).

Aluminium has a considerable influence on the kinetics and products of the process. Al-hydroxy cations promote hydrolysis of Fe²⁺ in solution and lead to precipita-

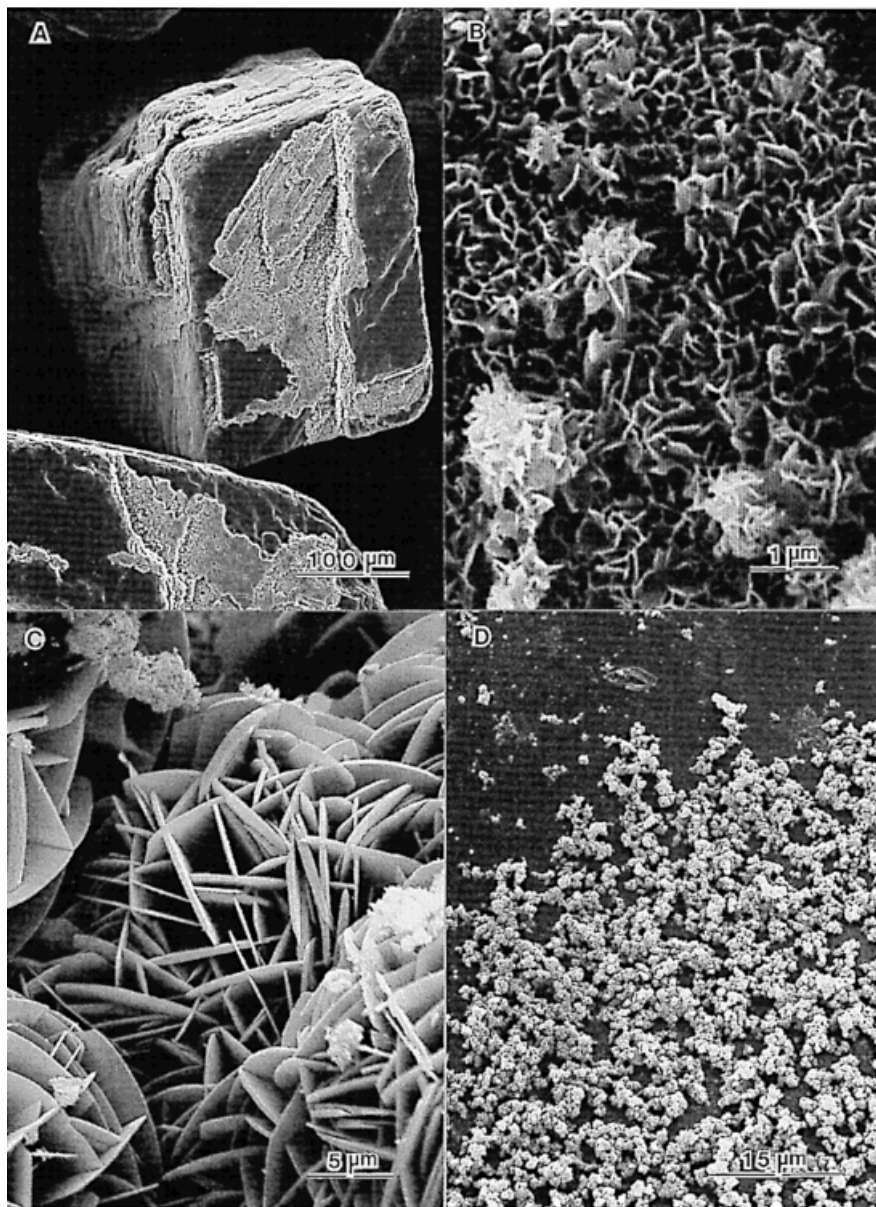


Fig. 13.8 Lepidocrocite and ferrihydrite deposits on calcite. A: Lepidocrocite with little ferrihydrite precipitated by rapid oxidation of 0.01 M $\text{Fe}(\text{ClO}_4)_2$ with purging of CO_2 -free air; B: Close-up view of A; C: Lepidocrocite formed by slow oxidation by $\text{O}_2/\text{N}_2 = 0.002$. D: Ferrihydrite precipitated from 0.01 M $\text{Fe}(\text{ClO}_4)_3$ (Loeppert & Clarke, 1984; with permission; courtesy R. Loeppert).

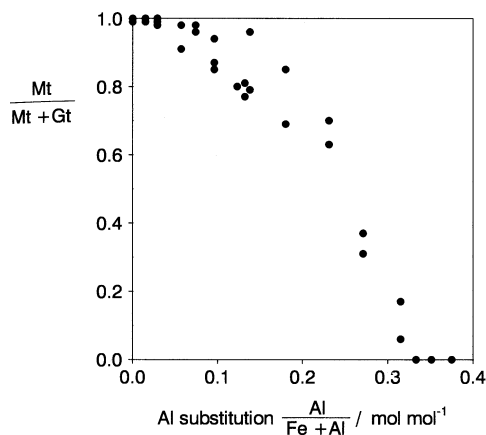


Fig. 13.9 Ratio between magnetite and goethite (Mt/(Mt+Gt)) as a function of Al in a system in which $\text{FeCl}_2/\text{AlCl}_3$ mixed solutions were oxidized slowly with air at pH 11.7 (Schwertmann & Murad, 1990, with permission).

tion of a solid phase at lower pH and lower $[\text{Fe}^{2+}]$ than would occur in the absence of Al; this process has been termed *induced hydrolysis* (Taylor, 1988). The green rust formed at $\text{Al}/(\text{Fe} + \text{Al})$ ratios of between 0.09 and 0.30 contains structural Al (Taylor & Schwertmann, 1978). Its oxidation rate is lower than that of pure green rust and it slows down production of Fe^{III} species. This is thought to favour formation of poorly crystalline, Al-substituted goethite over that of lepidocrocite. Al also suppresses formation of magnetite at pH 11.7 (RT) in favour of goethite (Fig. 13.9) (Schwertmann & Murad, 1990).

Fe^{II} solutions have been aerated at pH 7.2 in the presence of various *minerals* and *rocks* including quartz and basalt (Posey Dowty et al., 1986). The major product in all cases except that of quartz (goethite) was lepidocrocite. These authors also noted that lowering the dielectric constant of the solvent (by replacing water with a mixture of water and dioxane) promoted goethite over lepidocrocite. Poorly crystalline lepidocrocite was also the sole product when Fe^{2+} was oxidized at pH 7 and RT in the presence of bacteria (*Bacillus subtilis*; *Escherichia coli*) (Chatellier et al. 2001) (see also chap. 17).

13.4

Decomposition of Fe complexes

This process usually involves the hydrothermal decomposition (thermolysis) of Fe^{II} or Fe^{III} chelates to produce either hematite (under oxidizing conditions) or magnetite (reducing conditions). These chelates are extremely stable in highly alkaline media at low temperatures, but can be decomposed under hydrothermal conditions. This type of reaction is used to produce iron oxides of well defined morphology and size under controlled conditions. The soluble Fe-hydroxo species are slowly released until, when supersaturation with respect to an Fe oxide is exceeded, nucleation occurs; this is followed by an equilibrium growth stage. Fe and the ligand are present in more or less stoichiometric amounts so that when the complex breaks down, the

organic part is completely destroyed and does not interact with the growing iron oxide.

Booy and Swaddle (1978) produced magnetite by thermal decomposition of Fe^{II} and Fe^{III} complexes of aminopolycarboxylates (EDTA, nitrilotriacetate, methyliminodiacetate, iminodiacetate). These organic ligands provided a mildly reducing environment which prevented the formation of Fe^{III} oxides. Sapiieszko and Matijevic (1980) hydrothermally decomposed alkaline Fe-triethanolamine complexes to produce magnetite (in the presence of hydrazine) or hematite in the presence of KNO_3 . Hematite was also formed in alkaline KNO_3 /EDTA systems. Microcrystalline magnetite has been produced by heating at 300°C , Fe^{III} acetylacetonate in various organic solvents: l-propanol, ethanol, toluene, l-butanol and cyclohexanol. (Kominami et al. 1999). Around 1% (vol) water in l-propanol led to formation of hematite which, over 24 hr, was reduced to magnetite.

Morris et al. (1991) obtained "hematite" of very small particle size (~ 10 nm), termed "nanophase" by slow thermal decomposition in air of tri- Fe^{III} -acetato-hydroxy-nitrate. XRD shows only two broad lines as in a 2-line ferrihydrite, but the magnetic hyperfine field at 4.2 K of 50.4 T appears to be more in agreement with poorly crystalline hematite. Well-crystalline hematite and Al-hematite were produced by decomposing Fe-Al-oxinates at 700°C (da Costa et al. 2001).

14

Transformations

14.1

Introduction

A characteristic of the iron oxide system is the variety of possible interconversions between the different phases. Under the appropriate conditions, almost every iron oxide can be converted into at least two others. Under oxic conditions, goethite and hematite are thermodynamically the most stable compounds in this system and are, therefore, the end members of many transformation routes. The transformations which take place between the iron oxides are summarized in Table 14.1. These interconversions have an important role in corrosion processes and in processes occurring in various natural environments including rocks, soils, lakes and biota. In the latter environments, they often modify the availability and environmental impact of adsorbed or occluded elements, for example, heavy metals. Interconversions are also utilized in industry, e.g. in the blast furnace and in pigment production, and in laboratory syntheses.

These heterogeneous reactions are classified both on the basis of the chemical processes that occur and in terms of their structural features. Transformations without chemical changes are termed *isochemical*. Transformations that involve chemical modification are *dehydration* (loss of H_2O), *dehydroxylation* (loss of OH) and *oxidation/reduction* (a turnover of electrons). Structurally, the transformation processes are either topotactic or reconstructive (Mackay, 1961; Bernal & Mackay, 1965). A *topotactic* transformation takes place within the solid phase. It involves internal atomic rearrangements with a single crystal of the initial phase being transformed into a single crystal of another phase, i.e. there is agreement in three dimensions between the initial and final structures. Other solid state reactions in which the end product is not a single crystal, but there is, nevertheless, a clear relationship between the crystal axes of the final product and those of the reactant, are termed *pseudomorphic*. Because a solid-state transformation in the dry state requires a certain mobility of the atoms, it usually takes place only at elevated temperatures.

The second type of transformation, the *reconstructive* transformation involves dissolution/reprecipitation; the initial phase breaks down completely (dissolves) and the new phase precipitates from solution (for a review see Blesa & Matijevic, 1989). There is, therefore, no structural relationship between the precursor and the product. In contrast to the solid-state transformation, the reconstructive process is

Tab. 14.1 Interconversions among the iron oxides

<i>Precursor</i>	<i>Product</i>	<i>Type of transformation</i>	<i>Preferred medium</i>
Goethite	Hematite	Thermal or mechanical dehydroxylation Hydrothermal dehydroxylation	Gas/vacuum Solution
	Maghemite	Thermal dehydroxylation	Air + organic
Lepidocrocite	Maghemite, Hematite	Thermal dehydroxylation	Gas/vacuum
	Goethite	Dissolution/reprecipitation	Alkaline solution
	Magnetite	Reduction	Alkaline solution with Fe ^{II}
Akaganéite	Hematite	Thermal dehydroxylation	Gas/vacuum
	Goethite,	Dissolution/reprecipitation	Alkaline solution
	Hematite	Dissolution/reprecipitation	Acid solution
	Magnetite	Dissolution/reduction	Alkaline solution with N ₂ H ₄
δ-FeOOH	Hematite	Thermal dehydroxylation	Gas/vacuum
Feroxyhyte	Goethite	Dissolution/reprecipitation	Alkaline solution
Ferrihydrite	Hematite, Maghemite	Thermal dehydration/dehydroxylation	Gas/vacuum
	Goethite,	Dissolution/reprecipitation	Aqueous solution pH 3–14,
	Akaganéite,	“ “	Acidic media; presence of Cl
	Lepidocrocite	“ “	pH 6, presence of cysteine
	Hematite,	Aggregation, short-range crystallization within ferrihydrite aggregate	Aqueous solution at pH 6–8
Hematite	Substituted magnetite	Dissolution/reprecipitation	Alkaline solution with M ^{II}
	Magnetite	Reduction Reduction-dissolution reprecipitation	Reducing gas Alkaline solution with N ₂ H ₄
Magnetite	Maghemite, Hematite	Oxidation	Air
Maghemite	Hematite	Thermal conversion	Air
Fe(OH) ₂	Magnetite	Oxidation	N ₂ ; Alkaline solution
	Goethite, Lepidocrocite, Magnetite, Maghemite		Alkaline solution
FeO	Magnetite (+Fe)	Disproportionation	Air

driven by an energy gradient and depends on the solubility and dissolution rate of the precursor and can, therefore, take place under ambient conditions. It is, thus, the dominant process in many natural environments.

Ideally, a phase transformation should be investigated using a combination of techniques which enable changes in composition, structure, surface area, morphology and porosity of the solid phases and in the composition of the solution to be monitored, together with the reaction kinetics. This type of comprehensive investigation is rare for iron oxide interconversions; in most cases only one or two of the above aspects of the transformation have been considered.

This chapter is concerned with phase changes among the iron oxides as listed in Table 14.1.

14.2

Thermal transformations

14.2.1

General

The polymorphs of FeOOH and also ferrihydrite can be dehydrated to those of Fe₂O₃ under the influence of either heat or mechanical stress,



Although this type of transformation can take place in solution, usually under hydrothermal conditions, it has been most intensively investigated in the dry state. A precise separation of a transformation in the “dry state” from that in the presence of water is, however, often difficult because the minimum amount of water with which a via-solution transformation is still possible may be very small (see 14.3.5). This applies especially to poorly ordered and nano-sized oxides, such as ferrihydrite, with high surface areas and, therefore, high amounts of adsorbed water.

The end product of the dehydroxylation of pure phases is, in all cases, hematite,¹⁾ but with lepidocrocite, maghemite occurs as an intermediate phase. The amount of water in stoichiometric FeOOH is 10.4 g kg⁻¹, but adsorbed water may increase the overall amount released. Thermal dehydroxylation of the different forms of FeOOH (followed by DTA or TG) takes place at widely varying temperatures (140–500 °C) depending on the nature of the compound, its crystallinity, the extent of isomorphous substitution and any chemical impurities (see Fig. 7.18). Sometimes the conversion temperature is taken from thermal analysis data (e.g. DTA), but because of the dynamic nature of the thermoanalysis methods, the temperature of the endothermic peak is usually higher than the equilibrium temperature of conversion.

A common feature of the dehydroxylation of all iron oxide hydroxides is the initial development of microporosity due to the expulsion of water. This is followed, at higher temperatures, by the coalescence of these micropores to mesopores (see Chap. 5). Pore formation is accompanied by a rise in sample surface area. At temperatures higher than ca. 600 °C, the product sinters and the surface area drops considerably. During dehydroxylation, hydroxo-bonds are replaced by oxo-bonds and face sharing between octahedra (absent in the FeOOH structures; see Chap. 2) develops and leads to a denser structure. As only one half of the interstices are filled with cations, some movement of Fe atoms during the transformation is required to achieve the two thirds occupancy found in hematite.

Hematite derived from dehydroxylation of FeOOH at temperatures below 600 °C shows marked, non-uniform (differential) broadening of the XRD lines. Some authors have attributed this effect to the anisotropic shape of the coherently diffracting domains of hematite (Duvigneaud & Derie, 1980), and others to the development

1) At temperatures > 600 °C, ferrihydrite and also δ-FeOOH which have been partly substituted with divalent transition metals, transform to a

mixture of hematite and a spinel phase (Jiménez-Mateos et al., 1988).

of microstrains along the *c*-axis (Morales et al., 1984; Jiménez-Mateos et al., 1986). Differential line broadening of hematite obtained from goethite has also been attributed to incomplete ordering of the cations in the structure. The sharp lines are considered to be due to the oxygen anion framework which undergoes only slight structural rearrangement as goethite transforms to hematite, whereas the broader lines reflect a highly disordered cation arrangement (see next section) (Francombe & Rooksby, 1959; Brown, 1980). Upon heating above 600 °C, rearrangement of the cations occurs, the XRD lines sharpen and the pattern of well crystallized hematite with uniform line widths emerges. Another cause of differential line broadening is the preferential growth of the hematite crystal in the *a*-direction as compared to that in the *c*-direction. It has also been suggested that development of pores during low temperature calcination of goethite causes domains to develop and leads to broadening of the hematite peaks (Naono and Fujiwara, 1980; Baker et al. 2000). The latter authors found that differential broadening of the hematite XRD peaks was enhanced, if the goethite precursor was sulphated before being heated at 350 °C; this effect could be correlated with the formation of oriented pores and voids, but may also be due to structural disorder. The sulphate stabilizes the pores, especially the smaller ones, against agglomeration to meso pores on heating.

Maghemite produced by oxidation of isodimensional crystals of nano magnetite (<100–200 nm) shows uniform broadening of all XRD peaks due to the isotropic shape of the crystals, whereas the peaks of maghemite, if produced from goethite and lepidocrocite, are non-uniformly broadened due to their anisotropic crystal shape, and to the presence of stacking faults in their precursors, respectively (Morales et al. 1989). Furthermore, the maghemites from the FeOOH polymorphs contain some OH in the structure, whereas the ones from magnetite do not (Stanjek, 2000).

Thermal dehydroxylation of FeOOH has been studied both in vacuum and under various atmospheres. Kinetic studies of these transformations must be carried out under vacuum (Giovanoli & Brüttsch, 1974) and at a constant temperature. The temperature at which a phase transformation occurs, however, is determined by increasing the temperature of the sample in a controlled manner, i.e. by using a thermobalance (DTA or TGA method, see Chap. 7). Mechanical and mechanochemical dehydroxylation of FeOOH at room temperature can also be achieved by grinding.

Thermal transformation of the FeOOH polymorphs caused by natural or man-made fires is widespread in natural environments. The frequent occurrence of maghemite in surface soils of the tropics and at localized burning sites around the world, is due to the presence of organic matter which directs the transformation of goethite or ferrihydrite during heating, to maghemite, whereas in the absence of organic matter, hematite forms. Since reductants such as zinc powder or elemental sulphur also lead to maghemite formation from FeOOH upon burning (Van der Marel, 1951; Schwertmann & Heinemann, 1959), it is assumed that the transformation (FeOOH → maghemite) proceeds via magnetite. In fact with higher amounts of reductant, e.g. sucrose, and/or lower O₂ supply, magnetite instead of maghemite forms (Campbell et al., 1993). Anthropogenic maghemite may indicate prehistoric sites; it is detectable, even when underground, by using magnetic measurements (see Chap. 7).

14.2.2

Goethite to hematite

Decomposition of goethite to hematite by heating in the dry state has been followed by XRD, TEM, HRTEM, DTA, TG, synchrotron powder diffraction, constant rate thermal analysis and nitrogen adsorption (Goldsztaub, 1931; Bernal et al., 1959; Lima de Faria, 1963; van Oosterhout, 1967; Derie et al., 1976; Watari et al., 1979, 1983; Naono & Fujiwara, 1980; Paterson & Swaffield, 1980; Rendon et al., 1983; Schwertmann, 1984; Naono et al., 1987; Brendle & Papirer, 1998; Perez-Maqueda, 1999a, Ford & Bertsch, 1999, Gaultieri & Venturelli, 1999). Goethite proceeds directly to hematite without any intermediate phase. The transformation temperature usually depends on the crystallinity and Al substitution. For example, as the crystallinity of goethite improved, the endothermic (DTA) peak temperature shifted from 260 to 320 °C (Schwertmann, 1984). In addition, a double peak which is attributed to a two-phase transition of well-crystalline goethite to hematite developed (see Fig. 7.18). The double dehydroxylation peak has also been associated with high surface area samples (Derie et al. 1976), excess surface water (Goss, 1988) and the water vapour pressure (Perez-Maqueda, 1999a). In the latter case, a two-step transition occurred at a vapour pressure of ~ 3.5 mbar, whereas for the same sample at $5.5 \cdot 10^{-5}$ mbar there was only one step. Increasing Al-for-Fe substitution also leads to higher peak temperatures for dehydroxylation and to a splitting of the dehydroxylation endotherm (Schulze & Schwertmann, 1984).

The kinetic data for the dehydroxylation process, i.e. the degree of transformation, α , as a function of time could be fitted to both a random nucleation model, i.e.

$$-\ln(1 - \alpha) = kt \quad (14.2)$$

and to a three-dimensional diffusion controlled equation, i.e.

$$[1 - (1 - \alpha^{1/3})]^2 = kt \quad (14.3)$$

(Giovanoli et al., 1979). There is considerable scatter in the reported activation energies of dehydroxylation which range from 87.9 to 247 kJ mol⁻¹. This wide range appears to be related to the crystallinity and particle size of the sample (Giovanoli et al., 1979). The magnitude of even the lowest of these values is in line with a process in which the rate determining step is the chemical reaction.

The conversion of goethite to hematite is facilitated by the common anion framework shared by these two compounds. This remains more or less intact while water is lost and the cations are rearranged. Three unit cells of goethite form one unit cell of hematite. Thereby the crystal volume contracts by a factor of 0.62 as a result of a contraction of 25% in the [010] direction and an elongation factor of 1.2% in the [001] direction and of 3.7% in the [100] direction (Naono et al., 1987). X-ray diffractograms taken continuously during the transformation showed that the 210, 111, 211 and 212 lines of goethite shifted towards lower d-values and the 301, 400 and 401 lines moved to higher d-values. This indicates that the *b* edge length of goethite decreases and the

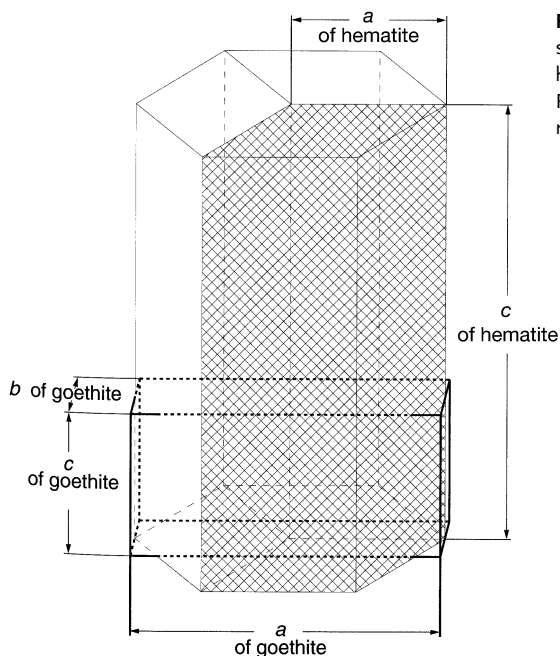


Fig. 14.1 Crystallographic relationships between the goethite and the hematite unit cells (Francombe & Rooksby 1959, modified; with permission).

a length increases just prior to the formation of hematite in line with the expected conversion (Schwertmann, 1984). Splitting of the DTA endotherm was attributed to this conversion. On the other hand, several shoulders at the low-temperature side of the peak, obtained in a high-resolution DTG instrument, were assigned to stepwise dehydroxylation-dehydration of surface $\text{Fe}(\text{OH}, \text{OH}_2)$ groups (Ford & Bertsch, 1999). The $[001]$, $[100]$ and $[010]$ directions of goethite become the $[001]$, $[010]$ and $[210]$ directions of hematite (Mügge, 1916; van Oosterhout, 1960) (Fig. 14.1).

The rearrangement of the Fe atoms during the transformation was inferred from differential broadening of the XRD peaks of hematite: all reflections except 110, 113 and 300, for which the structure factor depends on the position of the Fe atom, are broadened. This suggests that the peak broadening results from cation disorder (Pomies et al. 1998; 1999).

Hematite obtained at low temperatures retains the acicular morphology of the goethite precursor crystals, but at temperatures $> 600^\circ\text{C}$, a sintering process leads to irregular particles of hematite.

Morphological observations using TEM and HRTEM have provided further information about the mechanism of the reaction (Giovanoli et al., 1979; Watari et al., 1979, 1983; Naono et al., 1987). The HRTEM studies were carried out on mineral samples with *in situ* dehydroxylation being effected by the electron beam. A goethite crystal transforms into a mosaic of highly orientated hematite crystallites (< 5 nm across) separated by pairs of slit-shaped micro pores (0.8 nm wide) running along the goethite needle axis (Fig. 14.2a). HRTEM micrographs (Fig. 14.3a) show the development of these pores along the a -direction (Watari et al., 1979a). Water vapour

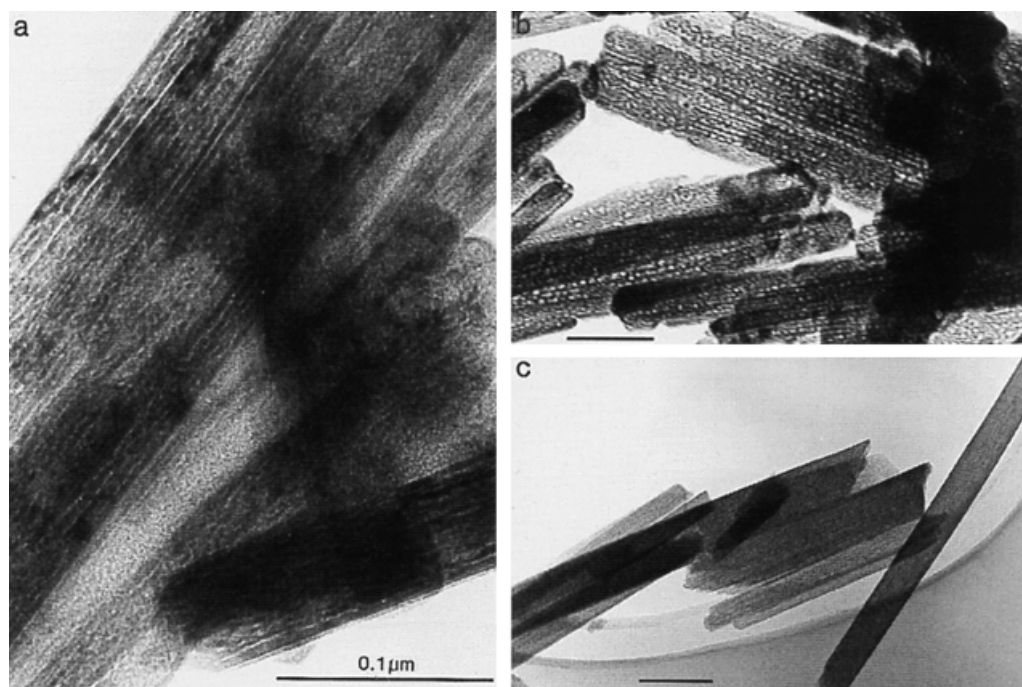


Fig. 14.2 Electron micrographs of heated FeOOH forms (courtesy H. Naono).

a) Pore structure of hematite produced by heating acicular goethite for 4 h at 300 °C in vacuo (Naono et al., 1987; with permission).

b) Pore structure of maghemite after heating

lath-shaped lepidocrocite for 3 h at 200 °C in vacuo (Naono & Nakai, 1989; with permission).

c) Akaganéite, heated for 20 h to 200 °C in vacuo and showing the slit-shaped ca. 1 nm wide pores running along [001] (Naono et al., 1982; with permission).

escapes via these pores. The hematite crystallites are twinned on the (100) plane. Hematite nucleation is confined to very small volumes of the goethite structure. It is induced by structural strain which arises from the dehydroxylation process and has to be accommodated by some structural rearrangement. Nuclei form initially at the surface of the crystal parallel to the (001) plane, in particular, in those areas where the ratio of surface area to volume is highest, i.e. at crevices and edges. Shielding the goethite surface with, for example, a coating of amorphous carbon, stabilizes it to much higher temperatures (Watari et al., 1979). HRTEM showed that there is a sharp boundary between the goethite lattice fringes ($100 = 0.9937$ nm) and those of hematite ($110 = 0.251$ nm) (Fig. 14.3b) with no evidence of any intermediate phase. Watari et al. (1979a), therefore, concluded that the superstructure¹⁾ postulated by earlier workers simply arose from diffraction by the periodic arrays of pairs of micro-

1) The existence of a superstructure was revealed by satellite spots in the XRD single crystal diffraction pattern of partly dehydrated goethite. The superstructure was considered to be an in-

termediate phase in which the iron concentration changed periodically in space (Lima de Faria, 1963).

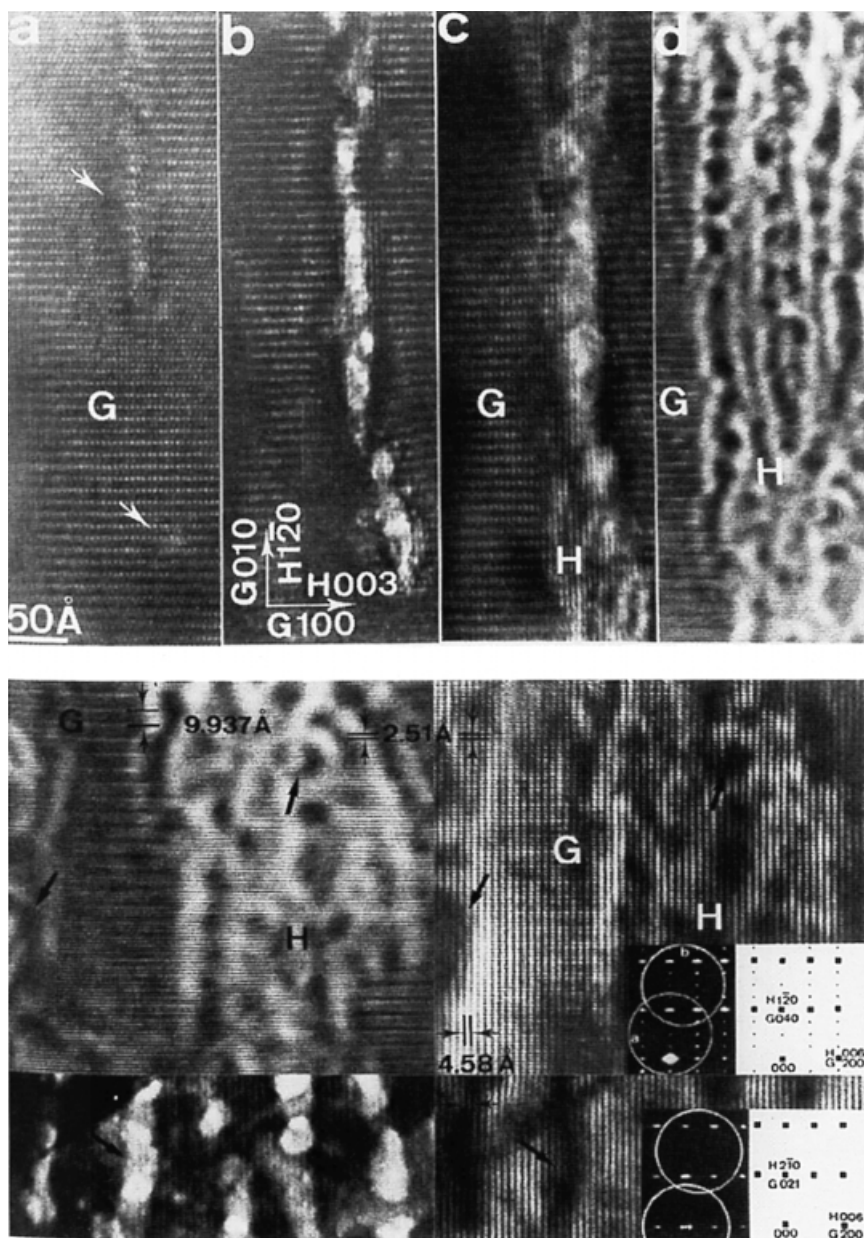


Fig. 14.3 High resolution electron micrographs of the thermal transformation of goethite to hematite showing (Gt[001]//[Hm[210] orientation. Upper: Gradual development (a $\Rightarrow$ d) of slit pores along Hm[001]. Lower: Largely transformed region along the (Gt[001]//[Hm[210] orientation. Electron diffraction patterns in the in-

set. Gt(010) fringes (0.9937nm) appear in every four layers of Hm(110) fringes (0.251nm); (left: bright field; right: dark field image). (Note that the hkl indices used for goethite are the previous ones) (Watari et al., 1979 a; with permission; courtesy J. van Landuyt).

pores and hematite crystallites. On continued heating at 250–300 °C, the hematite crystallites grow by a surface diffusion/coalescence process and the micropores are converted into mesopores. Acicular crystals of mesoporous, incompletely ordered hematite result. At temperatures >600 °C ordering is completed to give a fully crystalline material, the pores gradually disappear and the crystals sinter.

Goethite held in compressed discs of alkali halide dehydroxylates to hematite at between 250–500 °C (Yariv et al., 1980). Hematite is obtained at lower temperatures from these discs than from goethite alone and the transformation is faster in KI than in CsI discs. At higher temperatures, goethite can be reduced to maghemite (550 °C) and magnetite (>600 °C) in alkali iodide discs (Yariv et al., 1979; Mendelovici & Yariv, 1980). Goethite has also been converted to hematite by dry grinding in a ball mill (Mendelovici et al., 1982). Some hematite was noted by TEM and XRD after 16 hr of dry grinding goethite at room temperature and conversion was complete after 104 hr (Gonzales et al. 2000). During the transformation, striae of voids, attributed to dehydration, appeared on the surface of the goethite crystals. Ultimately the goethite needles (50 nm long) were converted to irregular, 20 nm hematite platelets.

14.2.3

Lepidocrocite to maghemite or hematite

Unlike goethite, lepidocrocite transforms upon dry heating first to maghemite and then to hematite (Hahn & Hertrich, 1923; Baudisch & Albrecht, 1932; Glemser, 1938; Takada et al., 1964; Giovanoli & Brüttsch, 1974, 1975; Gómez-Villacieros et al., 1984; Naono & Nakai, 1989; Gehring et al., 1990). (For the transformation of maghemite to hematite see section 14.2.7). The transformation temperature is between 200–280 °C in air and under vacuum drops to 120 °C (Fig. 14.4). The kinetic data was compatible with both a first order random nucleation model and with a diffusion controlled process: support for random nucleation comes from TEM observations. (Giovanoli & Brüttsch, 1974, 1975). The activation energy of this reaction is between 104 and 134 kJ mol⁻¹ and depends on sample surface area and crystallinity (Giovanoli et al., 1975).

The structural modifications at the beginning of the transition have been followed by magnetic, electron paramagnetic resonance and IR measurements. The magnetic susceptibility ($6.2 \cdot 10^{-7} \text{ m}^3 \text{ kg}^{-1}$ for the original lepidocrocite) increased abruptly after heating at 175 °C for 0.5 h indicating the formation of maghemite subunits and rose to a maximum of $12.6 \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ at 300 °C after the transformation to maghemite was completed, but then fell to ca. $3 \cdot 10^{-7}$ after heating to 700 °C when hematite was formed (Gehring & Hofmeister, 1994). Morris et al. (1998) reported corresponding values of 10, 402 and $0.2 \cdot 10^{-6} \text{ m}^3 \text{ kg}^{-1}$. The saturation magnetization increased from 0.3 to a maximum of $48.0 \text{ Am}^2 \text{ kg}^{-1}$ at the maghemite stage (265 °C) and then dropped to $0.1 \text{ Am}^2 \text{ kg}^{-1}$ at the hematite stage at 500 °C. These changes are reflected in the electron paramagnetic resonance spectra (Fig. 14.5) which show a significant increase in the asymmetric signal at $g \approx 2.5$ at 175 °C; the disappearance of this signal at higher temperatures can be attributed to hematite formation.

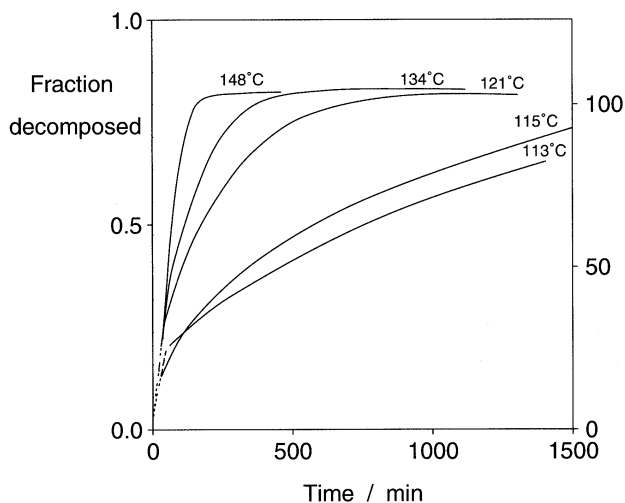


Fig. 14.4 Isothermal decomposition of lepidocrocite (specific surface area $14 \text{ m}^2 \text{ g}^{-1}$) in vacuum. (Giovanoli & Brüttsch, 1975; with permission)

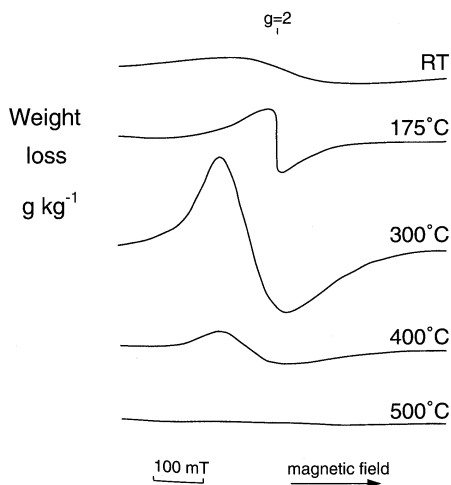


Fig. 14.5 Electron paramagnetic resonance spectra (EPR) of lepidocrocite at RT, and after stepwise heating to various temperatures (Gehring & Hofmeister, 1994; with permission).

TEM examination has shown that maghemite nuclei ca. 7 nm across (Fig. 14.2b) form in a random manner, initially at defects and crystal edges. Further strings of nuclei are then generated along the direction of the lepidocrocite lath axis (Giovanoli & Brüttsch, 1975; Naono & Nakai, 1989). Eventually, the original single crystal of lepidocrocite is replaced by a highly ordered aggregate of small maghemite crystals. The morphology of the original crystal is still maintained, with the [100] axis and (010) plane of lepidocrocite corresponding to the [011] axis and the (100) plane of maghemite. The transformation is thus, like that of goethite, pseudomorphic, rather

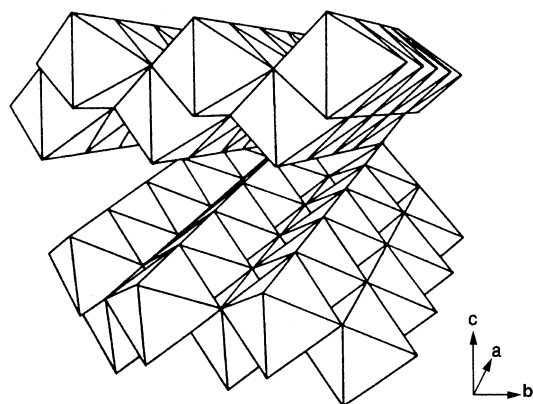


Fig. 14.6 Interface between intact lepidocrocite and collapsed layers (after dehydroxylation) forming maghemite (Giovanoli & Brüttsch, 1975; with permission).

than genuinely topotactic. Dehydroxylation is accompanied by a 29.1% and 4.3% contraction along [001] and [100], respectively, in the lepidocrocite unit cell and a 7.2% increase along [010] (Naono & Nakai, 1989). In other words, the corrugated layers of $\text{Fe}(\text{O},\text{OH})_6$ octahedra making up the lepidocrocite structure (see Fig. 2.5 d) collapse perpendicular to the b - c -plane thus inducing more corner and edge sharing as is found in the spinel structure (Fig. 14.6); this is accompanied by the formation and release of water (Giovanoli & Brüttsch, 1975). The formation of nuclei of maghemite enables the structure to accommodate the strain generated by this process. Even with a reaction time of weeks these crystallites do not increase in size, nor does the cation framework order completely. This is because crystallite formation is very rapid and once the lepidocrocite matrix has been disrupted, further diffusion and rearrangement of ions is blocked. As the decomposition reaction is promoted by the presence of water vapour, it is faster in air than under vacuum. In addition, the presence of water vapour induces nucleation of hematite, whereas under vacuum, the reaction does not proceed beyond the formation of maghemite (Giovanoli & Brüttsch, 1975); Chopra et al. 1999). Rietveld fits of the XRDs of lepidocrocite-derived maghemites indicate the presence of Fe-deficient sites which are charge-compensated by structural OH (Stanjek, 2000).

Lepidocrocite can also be converted to hematite by grinding in an agate mortar. Milling lepidocrocite in hexane or cyclohexane, however, led to partial conversion to maghemite together with small amounts of hematite (Fig. 14.7) (Gómez-Villacieros et al., 1984 a, 1987). The maghemite that forms appears to have an increased thermal stability.

14.2.4

Akaganéite and schwertmannite to hematite

Decomposition of akaganéite starts at 150 °C and complete conversion to hematite is achieved at ca. 500 °C. This is not a topotactic transformation; it involves a complete breakdown of the bcc anion packing of akaganéite followed by reconstruction of the hcp anion array of hematite. Initially, the product is in the form of elongated, porous

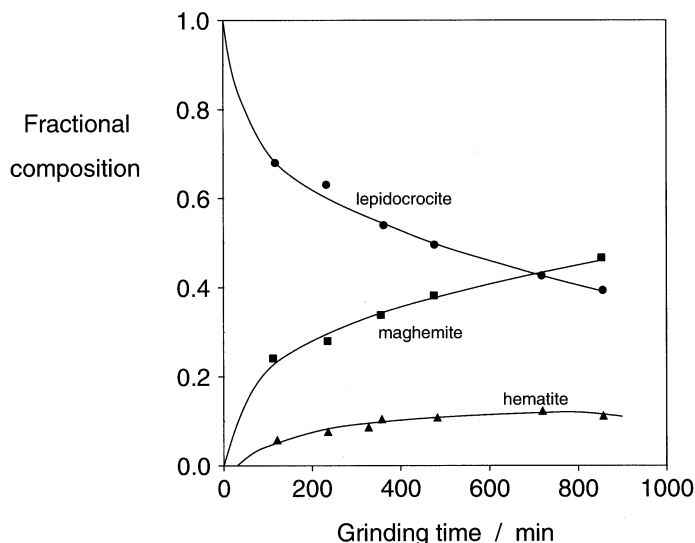


Fig. 14.7 Fractional conversion of lepidocrocite (surface area $122 \text{ m}^2 \text{ g}^{-1}$) to maghemite and hematite by dry grinding (Gomez-Villaceros et al., 1987; with permission).

crystals reminiscent of the akaganéite somatoids, but above 600°C , sintering to non-porous, rounded or hexagonal plates occurs. The extent of sintering depends to some extent on whether decomposition is carried out in air or under N_2 (Paterson et al., 1982; Naono et al., 1982). The decomposition temperature is very sensitive to the atmosphere under which the reaction is carried out, the reaction time and the level of water, chloride and substituting ions in the sample (Chambaere & De Grave, 1985). The higher the excess water content, the higher the transformation temperature. Chloride in the tunnels does not seem to retard dehydroxylation, but shifts the structural rearrangement leading to crystalline hematite to higher temperatures. The presence of structural Cu also stabilizes akaganéite against thermal decomposition (Inouye et al., 1974). Above 250°C , akaganéite releases water, the chloride content starts to decrease and HCl (under N_2) or Cl_2 (under O_2) is evolved. Above ca. 400°C , some FeCl_3 sublimates (Ishikawa & Inouye, 1975; Naono et al., 1982; Paterson et al., 1982).

The sample used by Naono et al. (1982) was a non-porous one (based on a t-plot) (Fig. 14.8) with a BET surface area of $22 \text{ m}^2 \text{ g}^{-1}$. It developed a maximum surface area of $178 \text{ m}^2 \text{ g}^{-1}$ at 200°C due to the formation of a system of slit-shaped pores ca. one nm wide (see Fig. 14.2 c). During this process, a contraction of ca. 30 % occurred along [100] and [010], but not along [001], i.e. not along the tunnels. With increasing temperature, the pores widened to mesopores and irregular macropores. The surface area of the hematite that finally formed at 500°C was only $23 \text{ m}^2 \text{ g}^{-1}$.

There is some uncertainty about whether akaganéite transforms directly to hematite. Some authors (Bernal et al., 1959; Dezsai et al., 1967; Morales et al., 1984) con-

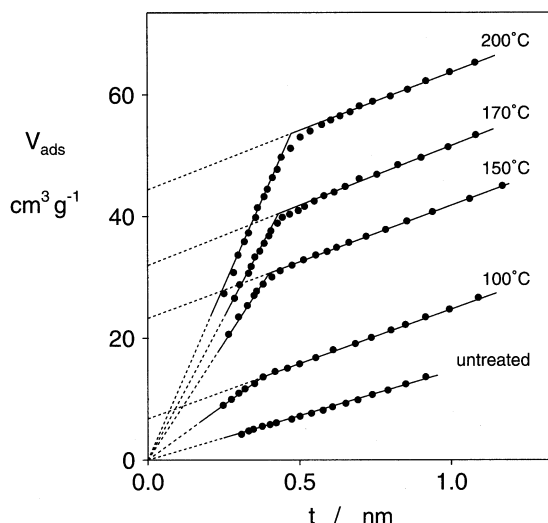


Fig. 14.8 *t*-plots for synthetic akaganéite heated to various temperatures for 20 h (Naono et al., 1982; with permission).

sider that hematite is the sole reaction product, whereas others claim to have detected an intermediate phase. Suggested intermediates include β - Fe_2O_3 , (Braun & Gallagher, 1972; Howe & Gallagher, 1975; Paterson et al., 1982), maghemite (Mackay, 1961; Galbraith et al., 1979; González-Calbet & Alario-Franco, 1982) and a poorly crystalline akaganéite indicated by the very broad and weak X-ray peaks (Ishikawa & Inouye, 1975; Naono et al., 1982; Chambaere & DeGrave, 1985). Whether an intermediate phase is produced may depend on the level of Cl in the sample (Nagai et al., 1980) or, alternatively on the atmosphere under which the transformation is carried out: in N_2 the transformation proceeded directly to poorly crystalline hematite, whereas in O_2 , an intermediate phase (β - Fe_2O_3) was observed (Paterson et al., 1982). Dry grinding of akaganéite leads to partial conversion to hematite (ca. 1/3 over 14 hours). The somatoidal crystals transformed into a more or less amorphous material (Barrios et al., 1986).

Upon heating in a DTA apparatus, schwertmannite first loses 15–20% of its weight which comes from both adsorbed water and structural $\text{OH}/\text{H}_2\text{O}$. At 540–580 °C, $\text{Fe}_2(\text{SO}_4)_3$ is formed by an exothermic reaction and transformation to hematite occurs via an endothermic reaction at ca 680 °C with release of gaseous SO_3 . Above this temperature, the crystallinity of hematite improves (Bigham et al., 1990; Bigham & Nordstrom, 2000). If exposed to the laser beam in a Ramanscope spectrometer, SO_4^{2-} is lost as SO_3 together with OH , but no $\text{Fe}_2(\text{SO}_4)_3$ is formed. The Fe atoms originally coordinated with SO_4^{2-} achieve tetrahedral coordination in maghemite (Mazzetti & Thistlethwaite, 2002).

14.2.5

 δ -FeOOH and feroxyhyte to hematite

On dehydroxylation of δ -FeOOH in the dry state or in solution, the end product is hematite. The platy morphology of the precursor is maintained with each plate decomposing into a porous aggregate of hematite crystals. Whether an intermediate phase precedes hematite appears to depend on the reaction conditions. Poorly crystalline δ -FeOOH transforms directly to hematite under vacuum and in air at 150 °C (Francombe & Rooksby, 1959; Mackay, 1961). Goethite or a goethite-like phase, appeared as an intermediate if δ -FeOOH was heated under an atmosphere with a high enough water vapour pressure, or heated in NaOH (Bernal et al., 1959; Feitknecht, 1959). Feitknecht et al., (1969) noted that the unit cell edge lengths of this intermediate phase did not exactly correspond to those of goethite. Although the cations and protons moved towards the goethite positions, the anion structure did not contract sufficiently for a perfect match – hence the intermediate could only be regarded as “goethite-like”.

As δ -FeOOH and hematite have a similar anionic framework (hcp), the conversion proceeds relatively easily. The mechanism involves outward diffusion of protons towards the surface of the crystals where combination with OH^- produces water. Simultaneously, cations migrate inwards and, as their concentration rises, they order on the octahedral vacancies to form hematite nuclei (Feitknecht et al., 1969). At a high enough temperature, there is a further loss of water followed by recrystallization of hematite. δ -FeOOH is converted to hematite fairly readily by dry grinding. Sintering during this process produces irregular hematite platelets that are much larger than the original crystals of δ -FeOOH (Jiménez-Mateos et al., 1988).

The thermal transformation of feroxyhyte (δ' -FeOOH) was studied by Carlson and Schwertmann (1980). Synthetic feroxyhyte transformed to hematite with non-uniformly broadened XRD lines at 240 °C (DTA). As the temperature increased further, an exothermic peak appeared and the crystallinity of the hematite improved. In an atmosphere of N_2 the transformation of natural feroxyhyte was impeded. As the temperature rose, the crystallinity of this feroxyhyte improved and at 460 °C, the a unit cell edge length dropped from 0.5062 to 0.5027 nm. As this sample contained organic impurities, the final transformation product in this case, even at 800 °C, was maghemite (see p. 368).

14.2.6

Ferrihydrite to hematite

The transformation of ferrihydrite to hematite by dry heating involves a combination of dehydration/dehydroxylation and rearrangement processes leading to a gradual structural ordering within the ferrihydrite particles in the direction of the hematite structure. This transformation may or may not be facilitated by the postulated structural relationship between the two phases. EXAFS studies have shown, for example, that some face sharing between FeO_6 octahedra, characteristic of hematite, also exists in 6-line ferrihydrite (see chap. 2).

Stanjek and Weidler (1992) and Weidler (1995) showed that 2- and 6-line ferrihydrite behaved quite differently upon heating. During heating at 127 °C for 1180 h, the ratio of $\text{H}_2\text{O}/\text{Fe}_2\text{O}_3$ decreased from 2.64 to 1.23 for a 2-line ferrihydrite and from 1.57 to 0.85 for a 6-line ferrihydrite without much change in the X-ray diffractogram. This means that considerable amounts of water can be expelled without there being any change in the structure of 6-line ferrihydrite. The oxalate solubility ($\text{Fe}_\text{o}/\text{Fe}_\text{t}$) paralleled the water loss and remained at 1.0 for the 2-line form, whereas for the freeze-dried 6-line material, it decreased from 0.27 to 0.16. The weight loss was linearly related to $(\text{time})^{-1/2}$ indicating a diffusion-controlled process, with the diffusion coefficient being three times higher for the 6-line than for the 2-line form. The N_2 -adsorption isotherms of the 2-line form (Fig. 14.9, upper) are type I with a gradual transition upon longer heating to type V (see Fig. 5.3). The surface area decreased slightly and the porosity rose markedly (ca. 55%). In contrast, the isotherm of the 6-line form (Fig. 14.9, lower) showed marked hysteresis with a common closure point at $p/p_0 \approx 0.4$ indicating the presence of pores of ca 4 nm across.

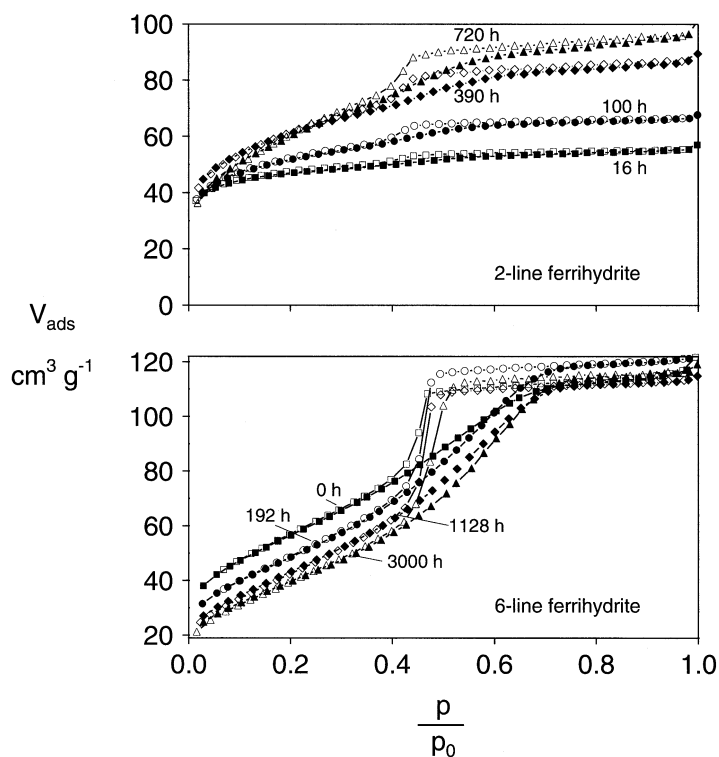


Fig. 14.9 N_2 isotherms of freeze-dried 2-line (upper) and 6-line (lower) ferrihydrites after heating for different lengths of time at 127 °C. Solid symbols: adsorption; open symbols: desorption (Weidler, 1995; with permission).

When 2-line ferrihydrite was heated at 227 °C or 327 °C, hematite formed readily and with increased heating time the closure point of the isotherms moved to higher p/p_0 . The gradual development of hematite at 227 °C is seen from the XRD-patterns (Fig. 14.10). During this transformation the surface area dropped from 203 to 125 m² g⁻¹ and the Fe_o/Fe_t from 0.27 to 0.12 while the closure point of the N₂ adsorption isotherms moved to higher p/p_0 (Weidler, 1995). Approximately one quarter of the ferrihydrite was converted to hematite after 9 h heating at 227 °C, whereas at 327 °C, complete conversion took place after 4 h. After 96 h heating at 427 °C, Fe_o/Fe_t had dropped to 0.024. Towe (1990) found that 6-line ferrihydrite was completely converted to hematite after heating at 400 °C for one hour. Small amounts of water have an important effect on the transformation: after outgassing for 6 hr, a 2-line ferrihydrite was stable up to 170 °C, whereas a sample exposed to the air for 1 hr at room temperature, during which it adsorbed water, transformed to hematite at 130 °C (Weidler, 1997).

It can be inferred from the gradual sharpening of all XRD peaks as the temperature increased, that a continuous increase in crystal size and order accompanies the decrease in weight and surface area (Stanjek and Weidler, 1992; Childs et al. 1993). If the effect of crystal order is neglected, the XRDs in Figure 14.10 would indicate an increase in crystal size (MCL_a) from 6.3 to 12.9 nm and a decrease in the unit cell volume from 0.30805 to 0.30291 nm³ after between 24 and 96 hrs of heating at 227 °C. The MCL_a of hematite produced by heating 2-line ferrihydrite increased from 24 (at

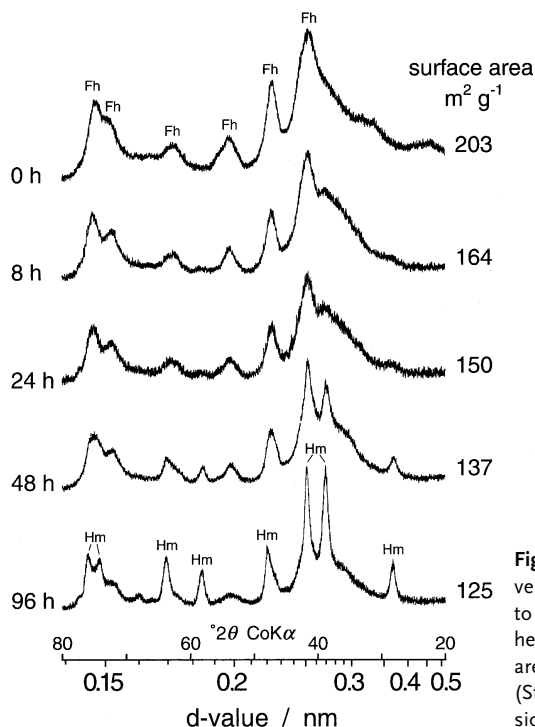


Fig. 14.10 X-ray diffractograms of conversion of freeze-dried 6-line ferrihydrite to hematite after between 8 to 96 h of dry heating at 227 °C. The decrease in surface area is shown on the right hand side (Stanjek & Weidler, 1992; with permission).

340 °C) to 126 (at 672 °C) and then to 700 nm (at 995 °C) and the MCL_c increased from 47 to 220 nm and then to $>10\ \mu\text{m}$. At the same time, the occupancy of Fe sites rose from 11.2 to 11.5 and then to 11.7 per unit cell (full occupancy = 12) indicating that the amount of OH in the structure had fallen over this temperature range (Campbell et al. 2002).

The mechanism of the transformation is still not fully understood. Stanjek and Weidler (1992) have suggested that as more and more hydroxyl groups in ferrihydrite are expelled, the average coordination number around Fe decreases, leading to charge imbalance and structural strain. Eventually a point is reached at which no more defects can be tolerated and a structural rearrangement (e.g. face-sharing) is initiated leading to hematite. The activation energy for the process is fairly high (390–500 kJ mol^{-1} ; Catlow et al., 1988) so the temperature must be high enough to permit sufficient cation diffusion. On the other hand, Watari et al. (1983) considered that the large amount of energy which is stored in the disordered, high surface area hematite is the main driving force for further ordering and for lowering the surface area. The release of this energy may also be responsible for the exothermic DTA peak (see sect. 7.10). The *gradual* increase in crystal size as indicated by XRD-peak sharpening (Fig. 14.10) appears to be in contrast to what occurs during the transformation of ferrihydrite to hematite in the presence of water where, from the very beginning of the transformation, relatively sharp lines appear and with time, only become more intense (see sect. 14.3.5).

Considerably higher temperatures are needed for the thermal conversion of ferrihydrite to hematite, if ferrihydrite contains foreign elements. A DTA experiment (heating rate 10 °C/min) showed that an increase in the Si/(Si+Fe) ratio from 0 to 0.153 in synthetic 2-line ferrihydrite produced by coprecipitation, caused the exothermic peak to shift from 331 to 778 °C and to become considerably weaker (Carlson and Schwertmann, 1981, Campbell et al. 2002). A mechanical mixture with SiO_2 did not exhibit this effect. Similarly, a 2-line ferrihydrite with a Si/(Si+Fe) mole ratio of 0.11 remained essentially unchanged after heating at 600 °C, but was completely converted to hematite at 850 °C (Glasauer et al. 2000). During this process, the characteristic IR Si-O band at $960\ \text{cm}^{-1}$ moved to 982 at 600 °C and to $1055\ \text{cm}^{-1}$ at 850 °C. Surface and structural (XPS) data suggest that Si is located at the surface where it hinders the rearrangement of Fe octahedra to hematite. On the other hand, unit cell measurements (XRD) of Si-containing hematite heated to 672 °C in a DTA instrument suggest that a and c increase as the Si/(Si+Fe) mole ratio increases from 0 to 0.07. This and a lowering of the number of Fe atoms per unit cell and the decrease in the B_{hf} at 4.2K from 54.03 to 53.32T, suggest that small amounts of Si are incorporated into the structure, probably compensating for the Fe^{III} deficit (Campbell et al. 2002). 2-line ferrihydrite precipitated in the presence of molybdate (concentration ratios of 0.05 and 0.35) likewise resisted conversion to hematite for up to 5 hr during heating at 300 and 500 °C (Zhao et al. 1994) as did a 6-line ferrihydrite with a Ge/(Ge+Fe) mole ratio of 0.17 at 700 °C. Natural Si-containing ferrihydrites with Si/(Si+Fe) mole ratios of 0.15–0.20 behaved similarly (Childs et al. 1993). Ferrihydrite, attached to a fully dehydrated SiO_2 surface, changed to maghemite on heating to 800 °C, whereas hematite was formed from ferrihydrite on a partly dehydrated SiO_2

surface (Ramesh et al., 2000). Maghemite, but no hematite was also formed on heating a gel produced from $\text{FeCl}_3 + \text{Si}(\text{OC}_2\text{H}_5)_4$ $\{\text{Fe}/(\text{Fe} + \text{Si}) = 0.07\}$ at up to ca. 1000°C (Ennas et al. 1998). It is likely that the maghemite (instead of hematite) owes its formation to the presence of organic carbon in this system.

14.2.7

Interconversions between maghemite and hematite

In the dry state, maghemite, depending on its origin and the content of foreign ions, transforms to hematite in the temperature range $370\text{--}600^\circ\text{C}$ (Bernal et al., 1959; Egger & Feitknecht, 1962; Feitknecht & Mannweiler, 1967; Sidhu, 1988; Tronc et al., 1990). As the transformation involves a change from a ccp anion arrangement to an hcp one, considerable rearrangement of the ions is required and hence a comparatively high temperature. The transformation is considered to be topotactic with the [111] and [110] axes of maghemite corresponding to the [001] and [110] axes of hematite, respectively (Feitknecht & Mannweiler, 1967). The large, lath-like particles of maghemite which formed from lepidocrocite, maintained the morphology of the original crystals upon conversion to hematite (Morales et al., 1989). Hematite nucleation occurs readily at crystal edges and corners; the nucleation energy is ca. 294 kJ mol^{-1} . The reaction can be blocked at lower temperatures by adsorption of phosphate which stabilizes ultrafine particles of maghemite to up to 800°C (Tronc & Jolivet, 1986). The transformation to hematite of maghemites containing $\leq 0.01\text{ mol mol}^{-1}$ Co, Ni, Zn, Cu, Mn, Al, V or Cr was retarded (Sidhu, 1988). The trace metals, apart from Mn and Cr, were ejected during heating and, as shown by dissolution studies, were concentrated in a surface layer (Sidhu et al., 1980).

The mechanism of the transformation appears to depend on crystal size (Feitknecht & Mannweiler, 1967). Ultrafine particles of maghemite (15 nm) transformed by a chain mechanism involving recrystallization of up to 100 particles to single, smooth edged, hematite flakes ca. $40 \cdot 70\text{ nm}$ in size. With larger crystals of maghemite (ca. 50 nm), there was a one to one transformation with one hematite nucleus forming and growing per crystal. If the maghemite crystals were greater than 70 nm across, nucleation was fast, but subsequent growth was slow and a function of the crystal size of the hematite already formed, whereas for intermediate sized crystals, the hematite nuclei grew rapidly.

Spindle-shaped maghemite, ca $0.03\text{--}05\text{ }\mu\text{m}$ in length was produced from spindle-shaped hematite by first reducing the latter to magnetite in a H_2 stream at 330°C for 6 hr and then oxidizing the magnetite in an air stream at 240°C for 2 hr (Itoh & Sugimoto, 2001). Dry grinding of hematite in a planetary ball mill led to a mixture of magnetite and wüstite (Randrianantoandro et al., 2001). If hematite (10 μm particles) were ground in ethanol, however, it was converted to 95% maghemite after 96 hr.

14.3

Via solution transformations

14.3.1

Lepidocrocite to goethite/hematite

Lepidocrocite transforms to goethite in acid Fe^{II} sulphate solution (Krause et al., 1934; Nitschmann, 1938; van Oosterhout, 1967; Bechine et al., 1982). The process involves a dissolution-reprecipitation mechanism and is promoted by the presence of Fe^{2+} ions which assist dissolution of lepidocrocite (see Chap. 12); the level of Fe^{2+} may be increased by addition of metallic iron to the system.

In alkaline media lepidocrocite transforms to goethite (Schwertmann & Taylor, 1972a). Goethite nucleates from soluble $\text{Fe}(\text{OH})_4^-$ species released by dissolution of lepidocrocite. Two important rate determining steps in this reaction are dissolution of the precursor and nucleation/growth of the goethite. Which step predominates appears to depend on the reaction conditions, particularly the temperature. Three different reaction vs. time curves could be obtained depending upon $[\text{KOH}]$ and temperature (Fig. 14.11). At 80°C and in 2 M KOH the kinetics were auto-acceleratory, indicating that nucleation and growth of goethite were rate determining, whereas at 20°C and in 0.1 M KOH, a deceleratory reaction governed by the rate of dissolution

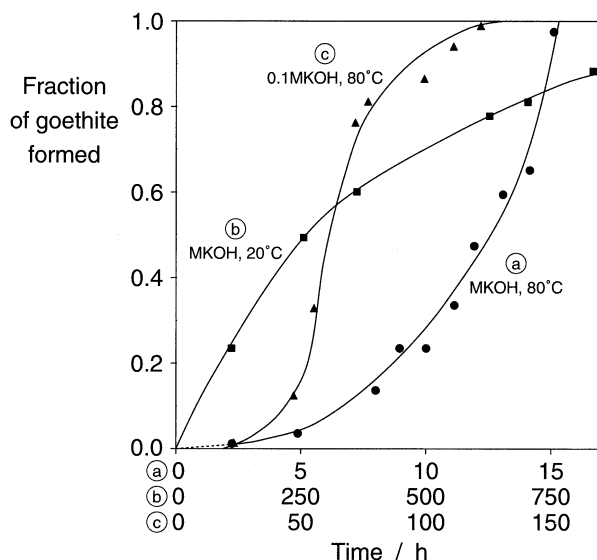


Fig. 14.11 Extent of conversion of lepidocrocite to goethite versus time in 1 M and 0.1 M KOH at 20 and 80°C . The following equations were used to calculate the solid lines (α = fraction of goethite formed; t = time): a: $\alpha = \exp(0.26 t - 3.93)$; b: $\alpha = 1 - \exp(-0.0025 t)$; c: $\alpha = [1 + 387 \exp(-0.093 t)]^{-1}$ (Schwertmann & Taylor, 1972a; with permission).

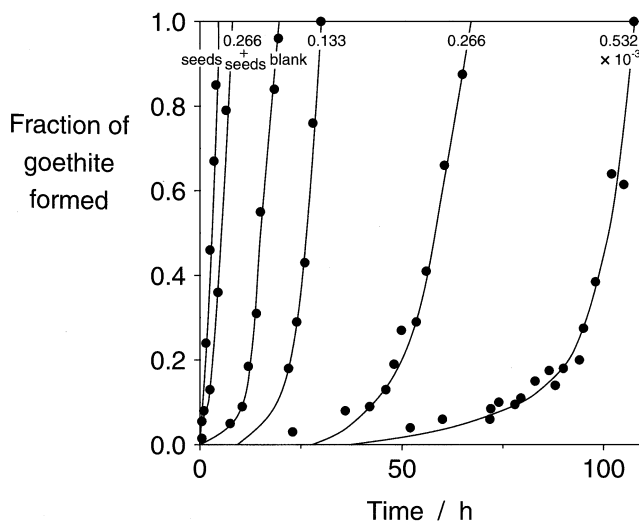


Fig. 14.12 The effect of silicate and seeding with goethite on the transformation of lepidocrocite to goethite in M KOH at 80°C . The figures on the curves give the Si concentration in mmol L^{-1} (Schwertmann & Taylor, 1972 a; with permission).

of lepidocrocite operated. Under intermediate conditions, both dissolution of the precursor and growth of the product contributed to the rate determining step and a sigmoidal plot resulted. At temperatures above 80°C and when the lepidocrocite sample was poorly crystalline, some hematite formed, possibly via a dehydroxylation process.

Silicate retarded the conversion reaction (Fig. 14.12). Seeding with goethite overcame the retardation if the Si/Fe ratio was low (0.008). At higher Si concentrations (Si/Fe = 0.2) dissolution of lepidocrocite as well as nucleation of the product was blocked (Schwertmann & Taylor, 1972; Cornell & Giovanoli, 1990). This can be overcome either by seeding with goethite or by adding Si after goethite formation has started. When goethite nucleation was blocked by silicate, the lepidocrocite partly dissolved and then recrystallized upon itself to form larger, cubic crystals. TEM observations showed that the thin, more soluble outgrowths of the lepidocrocite crystals (see Fig. 4.14b) dissolved and supplied soluble Fe^{III} species for recrystallization. It should be noted that at this high pH, recrystallization involved only Fe^{III} (not Fe^{II}) species.

14.3.2

Akaganéite to goethite/hematite

At temperatures of up to 70°C , akaganéite grown by hydrolysis of FeCl_3 is stable for months in the acidic mother liquor (Cornell, 1992). If, however, the system is seeded with goethite or hematite, the akaganéite gradually transforms into these com-

pounds (Atkinson et al., 1977). A solution of FeCl_3 heated at 99°C rapidly hydrolyses to akaganéite and this is converted over 100 to 200 hr to hematite via a dissolution/reprecipitation mechanism (Hamada & Matijevic, 1981, 1982). It is considered that a small proportion of hematite forms simultaneously with the akaganéite and serves as seed for the transformation. Without these seeds, hematite does not form (Blesa & Matijevic, 1989). The rate determining step in this conversion is considered to be the growth of hematite. High levels of ethylene glycol ($>400\text{ g L}^{-1}$) inhibit the conversion and smaller concentrations modify the morphology of the hematite that precipitates. Various methods by which acicular akaganéite is transformed via solution into spindle-like, uniform hematite particles have been reported (Sugimoto and Muramatsu, 1996; Itoh & Sugimoto, 2001).

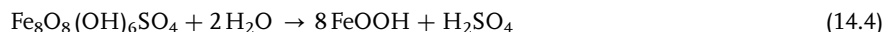
In alkaline media at 70°C , akaganéite also transforms to goethite and/or hematite (Cornell & Giovanoli, 1990). Goethite forms from akaganéite by a dissolution/reprecipitation process. It is the sole reaction product between $0.5\text{--}2\text{ M KOH}$, whereas outside this range some hematite forms as well (Cornell & Giovanoli, 1990); this variation with pH parallels what has been observed for ferrihydrite and lepidocrocite, i. e. akaganéite is just another source of Fe for hematite or goethite growth. Hematite precipitated as plates several microns across and much larger than the $0.3\text{ }\mu\text{m}$ somatoids of akaganéite. It has not been established whether hematite crystallizes from solution after dissolution of akaganéite or, alternatively, forms within aggregates of akaganéite crystals by a mechanism similar to that by which the ferrihydrite to hematite conversion proceeds (see 14.3.5). The shape of the plot of the extent of conversion vs. time was sigmoidal and the data fitted the Avrami-Erofejev law as did that for the dissolution of akaganéite in acid (Cornell & Giovanoli, 1988a, 1990). Seeding the system with goethite or hematite did not accelerate the reaction. Despite having a much higher specific surface area ($110\text{ m}^2\text{ g}^{-1}$ compared with $35\text{ m}^2\text{ g}^{-1}$), the rod shaped akaganéite crystals transformed to a more stable phase far more slowly than did the spindle shaped crystals (Fig. 14.13). These observations suggested that the rate determining step in the reaction is the dissolution of akaganéite.

As in the lepidocrocite $\Rightarrow$ goethite case, silicate species retard the transformation both by stabilizing akaganéite against dissolution and by interference in nucleation of the product. Seeding with goethite reduced, but did not entirely overcome, the effect of silicate species (Cornell & Giovanoli, 1990). Manganese, whether added as Mn^{2+} ions in solution or produced by dissolution of hausmannite (Mn_3O_4), retards the transformation (Fig. 14.13) by adsorbing on akaganéite and hindering its dissolution (Cornell & Giovanoli, 1991).

14.3.3

Schwertmannite to goethite

Schwertmannite is metastable with respect to goethite, except at very low pH (ca. <3) and in the presence of potassium when jarosite is stable. Schwertmannite, therefore, transforms spontaneously to goethite via solution at 25°C



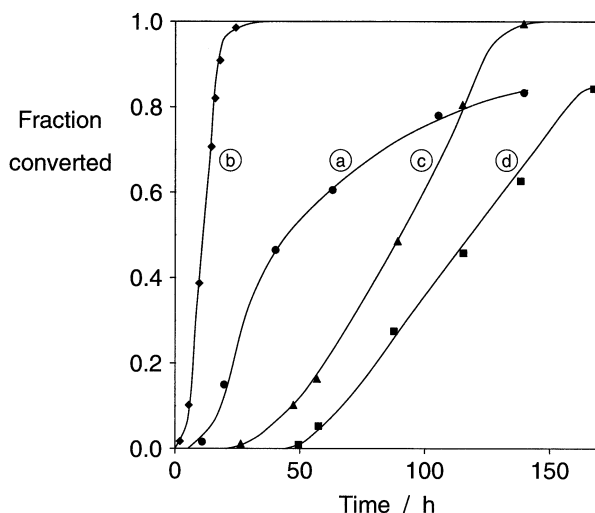


Fig. 14.13 Extent of transformation at 70 °C of akaganéite to goethite and hematite versus time. a) rod-shaped akaganéite in 1 M KOH; b-d) spindle-shaped akaganéite; b) 1 M KOH; c) 0.1 M KOH; d) 0.1 M KOH + Mn^{2+} ($\text{Mn}/(\text{Fe} + \text{Mn}) = 0.1$) (Cornell & Giovanoli, 1990, 1991; with permission).

releasing all its structural sulphate and producing protons (Fig. 14.14). The $[\text{SO}_4^{2-}]$ and $[\text{H}^+]$ in solution rose, whereas the $[\text{Fe}]$ increased initially and dropped once goethite formation started. In pure water at 25 °C, this transformation took about one year and goethite precipitated as small needles with a surface area of ca. $100 \text{ m}^2 \text{ g}^{-1}$ (Bigham et al., 1995). If the H_2SO_4 formed in reaction (14.4) is neutralized, as would often be the case in nature and in mine spoils, the rate of transformation to goethite increases as the pH of the system rises. In contrast, synthetic As- and Cr-schwertmannites did not transform to goethite at pH 4 even after one year (S. Regenspurg, pers. comm.).

14.3.4

Maghemite and goethite to hematite

Under hydrothermal conditions (150–180 °C) maghemite transforms to hematite via solution probably by a dissolution/precipitation mechanism (Swaddle & Oltmann, 1980; Blesa & Matijevic, 1989). In water, the small, cubic crystals of maghemite were replaced by much larger hematite rhombohedra (up to $0.3 \mu\text{m}$ across). Large hematite plates up to $5 \mu\text{m}$ across were produced in KOH. The reaction conditions influenced both the extent of nucleation and crystal morphology. The transformation curve was sigmoidal and the kinetic data in water and in KOH fitted a first order, random nucleation model (Avrami-Erofejev), i. e.

$$-\ln(1 - \alpha) = (kt)^n \quad (14.5)$$

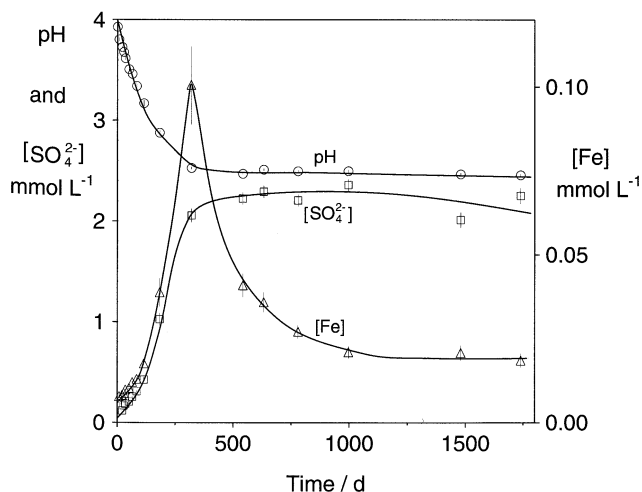


Fig. 14.14 Change in the concentration of Fe^{III} and sulphate and in pH during the transformation of schwertmannite to goethite in water at 25 °C. Vertical bars indicate one standard deviation (Bigham et al., 1996; with permission).

(see Chap. 12) with the value of n depending on the medium. In water, growth of hematite appeared to be the rate determining step, whereas in KOH, dissolution of maghemite governed the reaction. Silicate species ($\text{SiO}_2/\text{maghemite} = 0.2$ on a weight basis) retarded the transformation and in KOH suppressed hematite formation in favour of goethite (Swaddle & Oltmann, 1980); more goethite formed in NaOH than in KOH. As silicate adsorbs readily on iron oxides, the silicate species probably influenced the transformation by retarding the dissolution of maghemite and by interference in the nucleation of the products.

Under hydrothermal conditions at 180 °C, large hematite crystals form from fine-grained goethite. The goethite crystals first form aggregates each of which is then converted to a single, euhedral, hematite crystal (see Fig. 4.23c); the size of the hematite crystals seems to be strongly influenced by the size of the goethite aggregates indicating that the transformation takes place within these aggregates (Schwertmann, unpubl). The kinetics depend on crystal size: whereas goethite with a surface area of 116 m²/g had partly transformed at 250 °C and pH 6.5 ($p \sim 40$ atm) after 72 hr, goethite with a surface area of only 38 m²/g was unchanged. In parallel with the transformation to hematite, some goethite crystals simply grew bigger, mainly at the expense of the smaller crystals (De Grave et al. 1999). In neutral, aqueous media, goethite is stable to higher temperatures than in the dry state at ambient pressure: the stability range depends on the crystallinity of the goethite (De-Grave et al. 1999).

The dissolution of goethite in acidic media and the reprecipitation of the Fe as hematite, is a crucial process in the high-temperature leaching of nickel laterite ores. At 250 °C the rate of transformation increased as the Eh of the system was lowered

by the addition of FeSO_4 . This promoted reductive dissolution of goethite (Tindall & Muir, 1998).

14.3.5

Ferrihydrite to other Fe oxides

Numerous experiments have been carried out with ferrihydrite, predominantly the 2-line variety, which is a common precursor in the preparation of goethite and hematite. Certain additives, such as Fe^{2+} and other divalent transition metals and cysteine, can induce the transformation of ferrihydrite to green rusts, magnetite and even lepidocrocite (Table 14.1). Ferrihydrite can also be considered an important precursor for iron oxide formation in various natural surface environments. Hematite and goethite are both thermodynamically more stable than ferrihydrite and are by far the most common transformation products. Owing to their similar thermodynamic stabilities, goethite and hematite often occur together in the product. The proportion of each is determined by the reaction kinetics and hence the reaction conditions. Numerous investigations show that the two oxides form from ferrihydrite by competing mechanisms. For this reason, conditions that promote goethite are unfavourable for hematite and vice versa (Schwertmann & Murad, 1983). It now appears reasonably well established that the formation of goethite involves dissolution of ferrihydrite followed by crystallization of goethite in bulk solution, whereas hematite formation involves a combination of aggregation-dehydration-rearrangement processes for which water is required.

14.3.5.1 Rate of transformation

The transformation has been followed up by XRD, Mössbauer spectroscopy, EXAFS and colorimetry. It can be monitored more conveniently, however, by the acid oxalate extraction method in which residual ferrihydrite is dissolved and the crystalline product left intact (Schwertmann & Fischer, 1966). The extent of transformation at any time is given as the ratio Fe_o/Fe_t where Fe_o is the oxalate soluble iron (i.e. the unconverted ferrihydrite) and Fe_t is the total iron in the system. A plot of $\log (\text{Fe}_o/\text{Fe}_t)$ against time of aging at 100°C is linear over 90–95 % of the reaction

$$\log \text{Fe}_o/\text{Fe}_t = 0.0019 \cdot t \text{ (min)} + 0.166; \quad r^2 = 0.996 \quad (14.6)$$

indicating that first order kinetics are followed, i.e. the rate at any time is determined by the amount of ferrihydrite left. This type of plot has been found at temperatures ranging from room temperature to 100°C and at pH's of 4 to 13. The linear part of the curve does not extrapolate to zero time indicating that a nucleation stage precedes the main transformation (Schwertmann and Fischer, 1966; Schwertmann et al. 2000). This induction period can be reduced by addition of seed crystals of goethite or hematite with the latter serving as a seed for goethite growth. The induction period preceding hematite formation is not reduced by seeding with hematite, but can be reduced by adsorption of a hematite promoting agent such as oxalate or tartrate (Fischer & Schwertmann, 1975; Cornell & Schwertmann, 1979). By fol-

lowing the transformation of 6-line ferrihydrite to hematite in water at 92 °C and pH 2 with Mößbauer spectroscopy, Johnston and Lewis (1983) found that hematite was first detectable after 10 min and was the sole phase after 116 h. The main variation in hematite properties viz. an increase in MCL_{104} from 19 to 27 nm and in the magnetic hyperfine field at RT from 47.3 to 49.9 T took place within the first 2 hrs after only 50% conversion of ferrihydrite. No intermediate phases were detected.

Temperature and pH act on the rate of transformation in combination. Rises in both accelerate the reaction. At 4 °C the transformation took several years (Fig. 14.15), but only a few hours at pH 12 and 70 °C. The estimated activation energy for conversion of ferrihydrite to goethite is reported to range from 56.1 kJ mol⁻¹ at pH 11.7 to 48.2 kJ mol⁻¹ at pH 12.2 (Nagano et al., 1994). The rate of transformation increases as the pH of the system rises from 2 to 10; this is shown by a decrease in the half conversion time. At 24 °C, the time of half conversion decreased from 354 d at pH 2.5 almost linearly to <4 d at pH 10. At 50 °C and in the pH range 6.4–12.5, the rate constant, k , was found to be linearly related to $[OH]^{0.5}$ (Fischer, 1971) i.e.

$$k \text{ (min}^{-1}\text{)} = 1.7 \cdot 10^{-5} + 0.026 [OH]^{0.5} \quad (r^2 = 0.9994) \quad (14.10)$$

At 70 °C, the rate at pH 12 was far greater ($2 \cdot 10^{-3} \text{ min}^{-1}$) than at pH 8 ($8 \cdot 10^{-5} \text{ min}^{-1}$) (Cornell & Giovanoli, 1985; Cornell et al., 1989). Above pH 12 the rate levels out and above pH 13, decreases markedly. At very high pH, the overall transformation is retarded. At $[OH] > 4M$, large hematite crystals (several μm across) grew, indicating limited nucleation: the high negative charge on the ferrihydrite at this pH may hinder the aggregation step that must precede hematite formation (Cornell & Giovanoli, 1985). Small angle neutron scattering studies of the conversion products of ferrihydrite under hydrothermal conditions showed that the effect of pH on conversion time is similar to that at temperatures below 100 °C; at pH 4.5 conversion (to

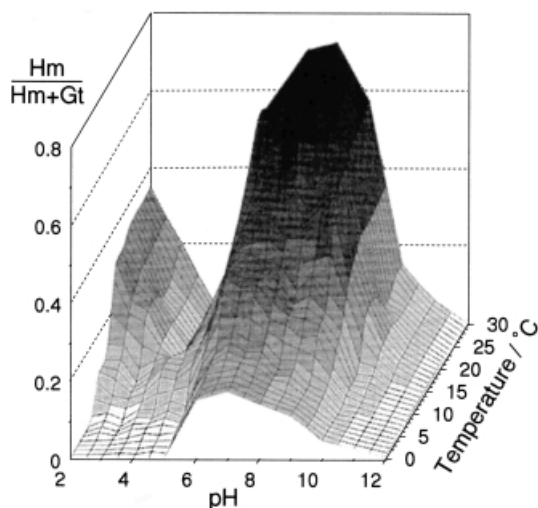


Fig. 14.15 The proportion of hematite formed from ferrihydrite in the pH range 2–12 and the temperature range 4–30 °C after 3392–4596 days of storage. The graph is interpolated from data at pH 2.5–12 in 1 pH unit steps and at 4, 10, 15 and 25 °C. Increasing hematite in the mixture is indicated by a darker shade (Schwertmann, unpubl.).

hematite) was completed in 4 h and at pH 10 (to a mixture of goethite and hematite) in 1 h (Nørlund-Christensen et al., 1983).

14.3.5.2 Hematite versus goethite formation

How factors such as the degree of ordering of ferrihydrite, and solution conditions, particularly pH and temperature affect the goethite/hematite ratio can provide information about the details of the process and also the conditions under which these two oxides might have formed in nature. The proportion of hematite formed after 15 hr at 100 °C increased from 43 % to 95 % as the temperature at which the ferrihydrite was precipitated rose from 0 to 100 °C (Schwertmann & Fischer, 1966). This suggests that with increasing temperature of precipitation, ferrihydrite dissolves less readily and the rate of dissolution (and hence goethite formation) falls.

As hematite formation involves a dehydration step, increasing the *temperature* promotes hematite at the expense of goethite (Van der Woude et al., 1983; Cornell & Giovanoli, 1985). This is observed even in the temperature range between 4 and 30 °C and is especially important around neutral pH (Fig. 14.15). The higher the temperature, the higher is the pH required to avoid hematite in the product (Fig. 14.16). The dominant factor that determines the goethite/hematite ratio is pH. Hematite predominates over goethite at around pH 7–8 over a wide temperature range (4 to at least 90 °C), whereas goethite is the sole product at pH 12–14. In fact, the oldest laboratory method of producing goethite (suggested by Böhm in 1925) consists of keeping 2-line ferrihydrite under 2 M KOH at 150 °C for 2 hr.

As the formation of goethite involves dissolution of the ferrihydrite, the proportion of goethite in the product parallels the solubility of ferrihydrite which is at a minimum at the pzc (around pH 7–8). As the *pH* moves in either direction from the pzc, the proportion of goethite increases, but at pHs <4 and >14, hematite again takes over. At very low and very high pH a speciation change – from monovalent to higher valent species which are less favourable for goethite formation, may outweigh

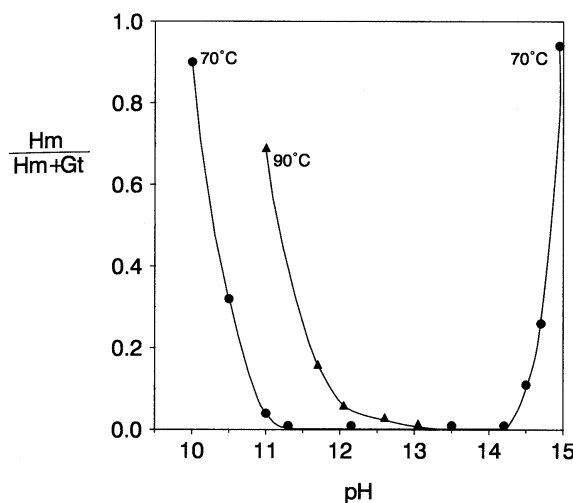


Fig. 14.16 Relationship between the hematite-to-goethite ratio ($Hm/(Hm+Gt)$) and pH at 70 °C and 90 °C after 24 h storage of 2-line ferrihydrite in KOH (Cornell & Giovanoli, 1985; with permission).

the increasing solubility of ferrihydrite (Schwertmann & Murad, 1983; Cornell & Giovanoli, 1985; Baltpurvins et al. 1996). Both at low (< 4) and high (> 12) pH, a hematite-promoting effect caused by increasing ferrihydrite concentration was also noted (Schwertmann & Fischer, 1966; Cornell & Giovanoli, 1985). After refluxing ferrihydrite for 4 hr in 0.05M KOH the proportion of hematite in the resulting goethite-hematite mixture increased almost linearly from 0 to 45% as the suspension concentration was raised from 1 to 10 g Fe L⁻¹ (Schwertmann & Fischer, 1966).

14.3.5.3 Mechanism of transformation

The transformation of ferrihydrite to better crystalline oxides may be regarded as involving competition between the processes by which goethite and hematite form. Goethite crystallization is straightforward nucleation/crystallization in the bulk solution. Growth involves small, soluble units, most probably Fe(OH)₂⁺ in the acid and Fe(OH)₄⁻ in the alkaline range (Feitknecht & Michaelis, 1962; Lengweiler et al., 1961, 1961a; Knight & Sylva, 1974). Monovalent species are regarded as the most suitable growth units because they need to lose only one unit of charge upon incorporation into the crystal. There is no evidence that in an acid medium, goethite forms by direct coalescence of chains of 1.5–3 nm particles into acicular goethite crystals, as suggested by Murphy et al. (1976b).

The mechanism by which hematite is formed from ferrihydrite in an aqueous system, appears more complicated than that by which goethite forms. If hematite crystals are added to the system they do not function as seeds for hematite formation but induce epitaxial growth of goethite instead (Atkinson et al. 1968; Cornell & Giovanoli, 1985).

Hematite forms by a combination of aggregation-dehydration-rearrangement process for which the presence of water appears essential. Structural details about this process at 92 °C were obtained from EXAFS (Combes et al. 1989; 1990): face-sharing between Fe octahedra developed before XRD showed any evidence for hematite. It is followed by internal redistribution of vacancies in the anion framework and by further dehydration. The dehydration process involves removal of a proton from an OH group and this in turn leads to elimination of a water molecule and formation of an oxo linkage. The local charge imbalance caused by proton loss is compensated for by migration and redistribution of Fe³⁺ within the cation sublattice.

A number of observations help to understand the mechanism of hematite formation from ferrihydrite in aqueous systems i.e. under conditions essentially different from those for solid-state transformation by dry heating (see 14.2.6). Air-dry storage of ferrihydrite containing 100–150 g H₂O/kg of water (found by weight loss) at room temperature for 20.4 years in closed vessels led to partial transformation to fairly well crystalline hematite with a little goethite (Schwertmann et al., 1999). In contrast, no hematite was formed from ferrihydrite if the content of adsorbed water was substantially reduced (Stanjek and Weidler, 1992; Weidler, 1997) as seen from the following examples:

(1) A 6-line ferrihydrite whose water content was reduced from 146 to 26 g kg⁻¹ by heating for 3000 hr at 123 °C, while the oxalate soluble proportion decreased from 100% to 12% and the unit cell volume from 0.3091 to 0.3079 nm³;

- (2) A 2-line ferrihydrite that had lost 150 g kg^{-1} of weight by heating at 170°C
- (3) A 2-line ferrihydrite, whose weight loss (at 800°C) was reduced to 48 g kg^{-1} by heating under vacuum for 20 hr at 177°C or for 6 hr at 223°C .

These results show that some (adsorbed) water is essential for the non-thermal conversion of ferrihydrite to hematite. TEM observations taken during the ferrihydrite $\Rightarrow$ hematite transformation have shown that the nano particles of ferrihydrite gradually coalesce to denser aggregates which eventually form single hematite crystals (Fig. 14.17). It is likely that hematite nucleation takes place in these ferrihydrite aggregates; the induction period corresponds to the agglomeration process. A corresponding observation was made for the transformation of poorly crystalline goethite

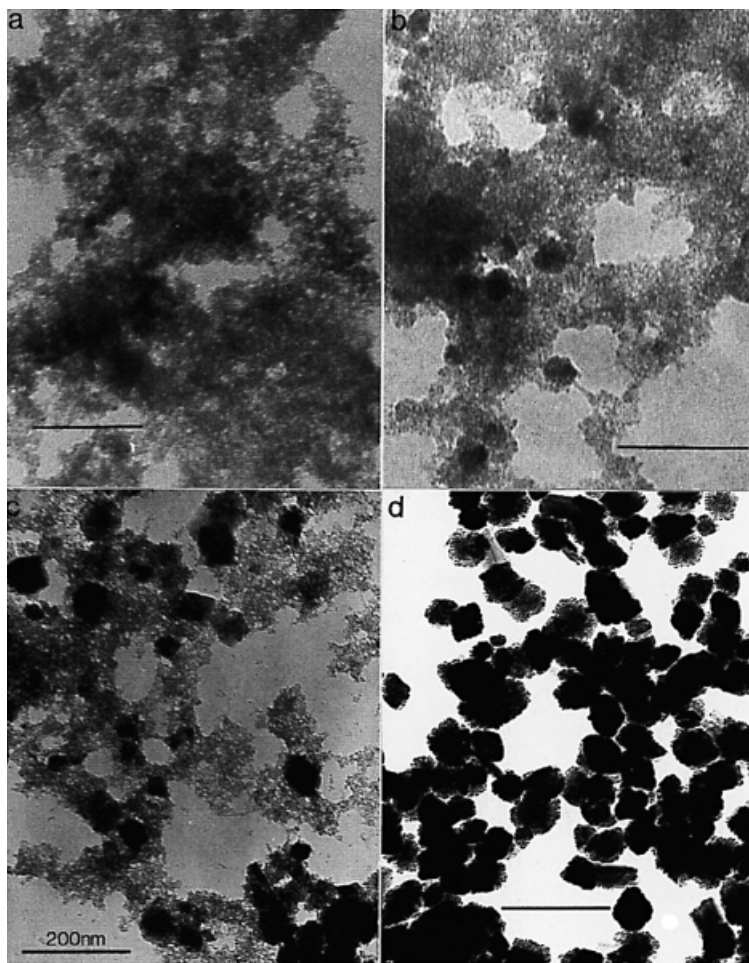


Fig. 14 17 Transmission electron micrographs documenting the transformation of ferrihydrite to hematite (Fischer & Schwertmann, 1975; with permission).

to hematite under hydrothermal conditions (Fig.4.23) (Schwertmann et al., 1999). In other words, aggregation appears to facilitate or even to be a prerequisite for hematite crystallization and, indeed, no hematite was formed from a stable sol held at pH 4 and 5 after 16–20 yr (!) at 24 °C (Schwertmann et al. 2000). This is in line with maximum hematite formation being around neutral pH, i.e. close to the zero point of charge where the solubility of ferrihydrite is at a minimum and aggregation is at a maximum. For the same reason, increased ionic strength at pH 12 (Cornell & Giovanoli, 1985; Cornell et al., 1987) and increased suspension concentration of ferrihydrite favoured hematite formation: the proportion of hematite increased from 0 to 80% (0.05 M KOH, 80 °C) as the ferrihydrite concentration rose from 1 to 40 g Fe L⁻¹ (Schwertmann & Fischer, 1966). It should be noted, that from the very beginning of the transformation in aqueous systems, the XRD peaks of hematite are relatively sharp, in contrast to the gradual peak sharpening observed during dry heating of ferrihydrite (Stanjek and Weidler, 1992; Schwertmann et al., 1999).

Direct proof for the participation of free water in the transformation to hematite was recently presented by Bao and Koch (1999): the oxygen of the hematite formed from 2-line ferrihydrite in the presence of water with a $\delta^{18}\text{O}$ of -8.0‰ had the same isotope ratio as this water, showing that the oxygen came predominately from the water present during the transformation and not from the ferrihydrite precursor.

In summary, there is considerable evidence to support the concept that in the presence of water, hematite forms from aggregated ferrihydrite by a *short-range crystallization process within the ferrihydrite aggregate*, with even adsorbed water being sufficient for the transformation to occur. The evidence is:

- (1) No hematite forms from sol particles, i.e. *aggregation* is essential
- (2) A minimum amount of *adsorbed water* is required (ca.100–150 g kg⁻¹ of ferrihydrite) below which no transformation takes place,
- (3) The transformation is preceded by a *nucleation* phase,
- (4) The hematite is reasonably *well crystalline from the beginning*, i.e. it does not show gradual ordering as in the dry heating process and,
- (5) ¹⁸O from the free water added to the system is found in the hematite structure.

14.3.5.4 Effect of foreign compounds

14.3.5.4.1 General

Foreign species refer to anions, cations and neutral molecules. Many of these species display a high affinity for the surface groups of the (high surface area) ferrihydrite and may, therefore, influence its transformation behaviour. On the basis of XAS, it has been suggested that the surface adsorbed H₂O, which completes the surface Fe coordination, forms sites of crystallization and that these sites may be blocked by additives such as silicate (Zhao et al., 1994a). Some of these species stabilize ferrihydrite for long periods of time and this is important in sediments, soils and living organisms (see Chap. 15, 16 and 17, respectively). Table 14.2 lists the foreign species studied to date. The investigations referred to here, were, in general, carried out at pH's ranging from the slightly acid to the extremely alkaline and at temperatures of between 25–100 °C. The ratio of additive, A, to Fe in the system (A/Fe) was usually between 0.001 and 0.1.

Tab. 14.2 Foreign compounds whose influence on transformation of 2-line ferrihydrite in aqueous systems has been investigated (for trace metals see also chap. 2)

<i>Foreign compound</i>	<i>Reference</i>
Carboxylic and hydrocarboxylic acids	Schwertmann et al., 1968; Fischer & Schwertmann, 1975; Cornell & Schwertmann, 1979; Kandori et al., 1991a
Sugars, glycerol	Cornell, 1985; Taylor et al., 1987
Silicate	Anderson & Benjamin, 1985; Cornell et al., 1987; Cornell & Giovanoli, 1987; Quin et al., 1988; Vempati & Loeppert, 1989; Kandori et al., 1992; Glasauer, 1995; Campbell et al. 2002
Phosphate	Reeves & Mann, 1991; Kandori et al., 1992; Barron et al. 1997; Galvez et al. 1999
Arsenate	Ford, 2002
Humic/fulvic acids	Schwertmann, 1966; Kodama & Schnitzer, 1977
Reducing organic ligands	Cornell & Schneider, 1989; Cornell et al., 1989 a, 1989 b, 1990, 1992
Clay minerals	Schwertmann, 1979; 1988; Schwertmann et al. 2000a
Al	Lewis & Schwertmann, 1979, 1979 a; Torrent et al., 1982; Schulze & Schwertmann, 1984; Schwertmann et al. 2000
Ti	Fitzpatrick et al., 1978
Mn	Stiers & Schwertmann, 1985; Cornell & Giovanoli, 1987; Cornell, 1988; Cornell et al., 1990; Cornell, 1991
Cr	Schwertmann et al., 1989
V	Schwertmann & Pfab, 1994
Ni, Co, Zn	Cornell, 1988; Cornell & Giovanoli, 1989; Giovanoli & Cornell, 1992; Ford et al. 1999
Pb	Ford et al. 1999
Cu	Inouye et al., 1971, 1972; Cornell, 1988; Cornell & Giovanoli, 1988
Nd	Nagano et al. 1999

In general, foreign species in the system can have two different effects on the transformation of ferrihydrite to other Fe oxides; they can either modify the rate of the transformation, usually by slowing the process, or change the composition (mainly the hematite/goethite ratio) and properties of the end product. Two principal mechanisms of interaction operate:

- The foreign species are retained by the ferrihydrite either via adsorption (ligands) or by structural incorporation and thereby suppress, or more rarely, raise its reactivity towards internal ordering and/or dissolution.
- The foreign species act in solution and usually retard nucleation or growth of goethite by competing with soluble Fe^{III} species for sites on the subcritical nucleus or on the growing crystal. This mechanism is independent of the presence of ferrihydrite.

The effects of foreign species (especially retardation) are particularly strong at room temperature where the transformation may be retarded for months or even years; they become weaker as the temperature rises. For this reason, most results discussed here were obtained at elevated temperatures.

14.3.5.4.2 Anions and neutral molecules

The effect of the anion which accompanies the Fe^{III} salt, on the transformation is small and follows the order $\text{NO}_3 < \text{Cl} < \text{SO}_4$ (Baltpurvins et al. 1996). The effect of weakly complexing organic ligands which act in solution, e.g. lactate, simple amino acids and molecules such as sucrose is also weak and can be overcome by seeding the system with a few percent goethite crystals; this has no effect, however, on strongly complexing ligands such as tartrate which *adsorb* on ferrihydrite (Cornell, 1985). Because foreign ions which act only in solution have no *direct* influence on hematite formation, the level of this phase in the product rises simply because the rate of goethite formation is suppressed.

Ligands which adsorb on ferrihydrite have a far greater effect than those that act solely in solution. The extent of adsorption and hence, the effect on the transformation, depend on the pKs of the ligands, the type and number of functional groups and on steric factors (see chap. 11). Acyclic molecules such as citrate and sorbitol stabilize ferrihydrite to a greater extent (at the same A/Fe) than do cyclic molecules with the same functional groups (Cornell, 1985). Adsorbed ligands usually retard the overall transformation of ferrihydrite, although there are some which accelerate hematite or goethite formation. Where the overall crystallization rate is reduced, the rates of formation of both goethite and hematite are retarded.

An increase in the proportion of hematite in the product indicates that the rate of goethite formation is reduced to a greater extent. Adsorbing ligands retard goethite formation by stabilizing ferrihydrite against dissolution. Such ligands tend to be polydentate and adsorb on ferrihydrite via binuclear, inner-sphere complexes. Hematite formation may be retarded because the aggregation of the ferrihydrite particles, necessary for hematite formation, is blocked. The organic ligands either link the particles into an immobile network or increase the electrostatic repulsion between the particles (Cornell & Schwertmann, 1979; Cornell, 1987; Cornell et al., 1989). Infrared studies showed that those organic ligands e.g. oxalate and tartrate which accelerate hematite formation adsorb on ferrihydrite through a pair of functional groups separated by one carbon-carbon bond (Fig.14.18) (Parfitt et al., 1977; Cornell & Schindler, 1980). The oxalate surface complex is believed to induce formation of areas of local or-

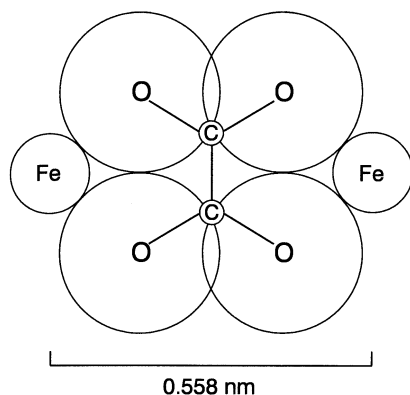


Fig.14.18 Schematic presentation of the Fe-oxalate molecule showing the Fe-Fe distance of 0.558 nm (Fischer & Schwertmann, 1975, with permission).

dering within the ferrihydrite particles because their Fe-Fe distance (0.558 nm) is very similar to the Fe-Fe distance in hematite (0.542 nm) (Fischer & Schwertmann, 1975).

Inorganic poly-valent anions that form strong (innersphere) complexes with the ferrihydrite surface markedly retard the transformation. The most important species are silicate, phosphate, and arsenate. Silicate strongly adsorbs at a low Si/Fe of 0.005 and at a high pH of 12 (where the ferrihydrite surface is negatively charged) and thereby promotes hematite formation over that of goethite (Fig. 14.19). Although seeding with goethite overcame the effects of very low levels of silicate (Si/Fe = 0.0001), it was not effective at higher Si concentrations indicating that this ligand operates by stabilizing ferrihydrite against dissolution (Cornell et al., 1987; Cornell & Giovanoli, 1987). Where silicate does not block the dissolution of the precursor, its main action is in solution where it interferes with nucleation of goethite. At room temperature and a pH of 12.5, there was 55% conversion to goethite after 660 d in the presence of 0.01 M silicate, but none with 0.1 and 1 M silicate; addition of goethite at high [Si] had no seeding effect (Cornell & Giovanoli, 1987; Glasauer et al. 1999). Natural ferrihydrites precipitated in cold surface waters frequently contain a few per cent Si which may, in fact, be the reason for their long-term stability (Carlson and Schwertmann 1981). Phosphate coprecipitated with ferrihydrite at a P/Fe mol ratio of up to 0.03 promoted hematite over goethite and lepidocrocite at between pH 3 to 6 at 25, 45 and 100 °C (Galvez et al. 1999), and similarly, at a P/Fe ratio of up to 0.025 retarded the transformation over the pH range 9–12 at 50 and 100 °C (Barron et al. 1997). Likewise, arsenate hinders the transformation at pH 6 and 40 °C and promotes hematite over goethite (Ford, 2002).

In geoenvironments where Si and Al is supplied by silicates and clay minerals, Fe oxides are often formed in the presence of these minerals. A long term experiment in which synthetic 2-line ferrihydrite was held at pH 5 and RT in the presence of common clay minerals showed that after 8.4 years the degree of transformation (to a mixture of goethite and hematite) was between 0 and 96 % (Schwertmann, 1988a). It decreased in the order, control > gibbsite > illite > kaolinite > smectite > soil smectite > allophane. The silicate concentration increased (to 5.9 $\mu\text{g L}^{-1}$) along the series in this order suggesting that silicate retarded or blocked the transformation. During

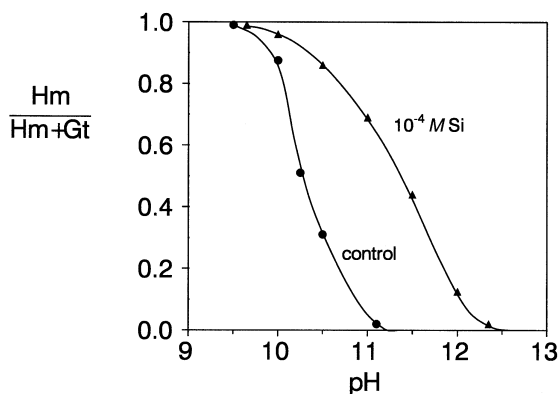


Fig. 14.19 The effect of silicate (Si/Fe = 0.005) on the transformation of 2-line ferrihydrite into goethite and hematite at 70 °C (Cornell et al., 1987; with permission).

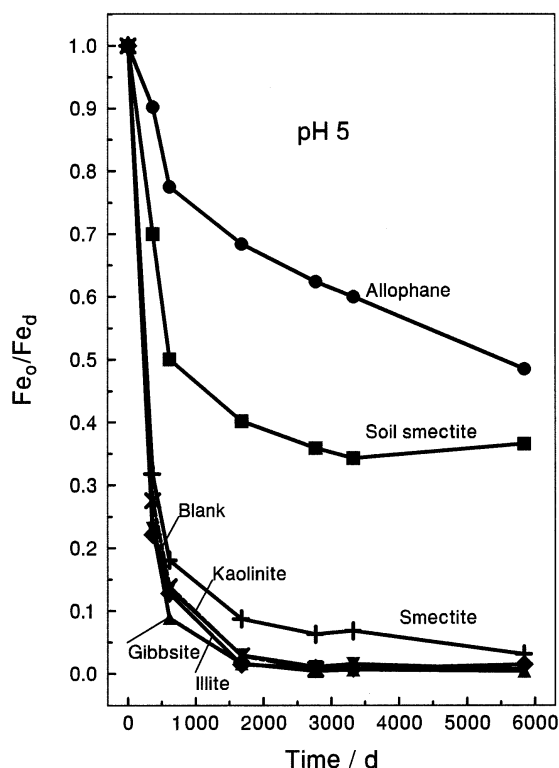


Fig.14.20 Effect of various clay minerals on the transformation of 2-line ferrihydrite to goethite and hematite at 25 °C and pH 5 after 16 yr as measured by the ratio of oxalate to dithionite soluble Fe (Fe_o/Fe_d) (Schwertmann et al. 2000 a, with permission).

16 yr of aging at 25 °C and at pH 4; 5; 6 and 7, allophane and a poorly ordered soil smectite stabilized a proportion of ferrihydrite, whereas the better crystalline clay minerals, such as kaolinite and illite did not (Fig.14.20). This may be due either to the reduced activity of the remaining ferrihydrite, or to retarded nucleation and crystal growth of goethite/hematite, both caused by Si and Al released from the clay minerals. The more active minerals, especially allophane, also promoted hematite over goethite and released some Al into solution which was then partially incorporated into the Fe oxide structure (Schwertmann et al. 2000 a). The resistance of some natural ferrihydrites (which often contain several per cent of carbon) to transformation may also be due to attached organic molecules (humics).

Cysteine ($\text{SCH}_2\text{HNH}_2\text{OOH}$), a reducing organic ligand, has the unusual ability to induce rapid conversion of ferrihydrite to goethite or lepidocrocite at a pH at which, in the absence of the ligand, hematite is the predominant product (Cornell & Schneider, 1989; Cornell et al. 1989 a, b). Interaction of cysteine with ferrihydrite involves adsorption through the carboxyl and sulphhydryl (reducing) groups. This is followed immediately by a reduction of a proportion of the interfacial Fe^{III} ions together with simultaneous oxidation of cysteine to its disulphide (cystine). The mixed valence compound dissolves more readily than ferrihydrite and, this facilitates the formation of FeOOH . The reaction products depends upon the cysteine/Fe ratio and on the buf-

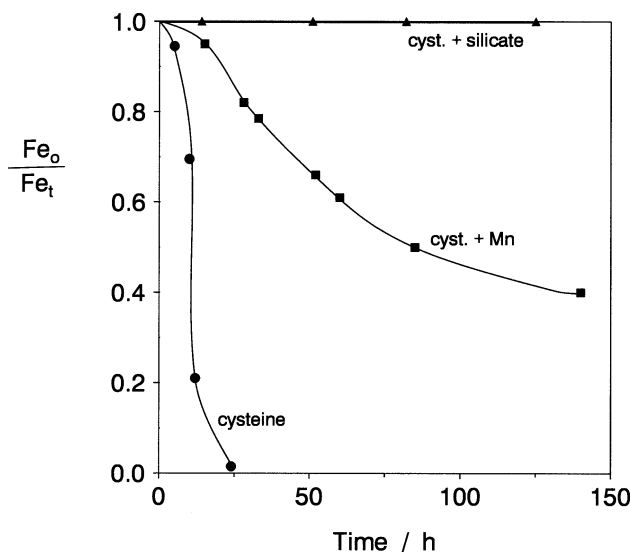


Fig. 14.21 Effect of cysteine (cyst) alone and cysteine + silicate ($\text{Si}/\text{Fe} = 0.1$) or cysteine + Mn ($\text{Mn}/(\text{Fe} + \text{Mn}) = 0.1$) on the transformation of 2-line ferrihydrite to goethite (Cornell, unpubl.)

fering agent in the system. For FeOOH to form, the cysteine/Fe ratio must be > 0.1 ; at lower ratios the stabilizing effect of cysteine (through two adsorbing functional groups) outweighs the surface-Fe reduction and eventually hematite forms. Phosphate and silicate adsorb on ferrihydrite in preference to cysteine and thus reduce its goethite promoting effect (Cornell & Schneider, 1989) (Fig. 14.21). Coprecipitated Mn^{2+} has the same effect; it appears to act, however, by diluting the surface $[\text{Fe}]$ and hence the proportion of interfacial Fe^{2+} (Cornell et al. 1990).

14.3.5.4.3 Cations

Cations differ from ligands in that they influence the crystallization of ferrihydrite over a wider pH range than do ligands. They usually require mol ratios ($\text{M}/(\text{M} + \text{Fe})$) of 0.05–0.1 to influence the kinetics and products of the reaction, whereas ligands are often effective at hundredfold lower concentrations. In addition, cations are often incorporated in the iron oxide structure (see Chap. 3). The effects of Al^{3+} , Ti^{4+} , V^{3+} , VO^{2+} , Pb^{2+} , Cr^{3+} , and the first row divalent transition elements have been investigated. These effects vary widely, although retardation predominates.

The influence of aluminum has been studied intensively (Gastuche et al., 1964; Fey & Dixon, 1981, workers in the alumina industry and a series of publications by Schwertmann & coworkers). The rate of transformation of coprecipitated Al-ferrihydrite to goethite/hematite at 25 °C and pH 4; 5; 6 and 7 was reduced from ca. 1 to 0.03 yr^{-1} as $\text{Al}/(\text{Fe} + \text{Al})$ in the system increased from 0 to 0.1 (Schwertmann et al. 2000). The effect becomes less as the pH rises. Coprecipitated Al had a greater effect

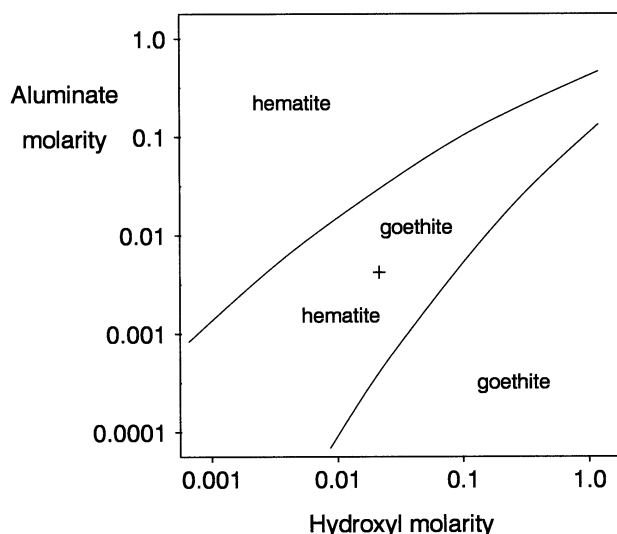


Fig. 14.22 Fields of formation of goethite and hematite from Al-ferrihydrite at 70 °C as a function of [OH] and [Al] (Lewis & Schwertmann, 1979 a; with permission).

than Al that was added after precipitation (Lewis & Schwertmann, 1980). Coprecipitated Al retards the transformation by hindering the dissolution of ferrihydrite and also interferes with nucleation/growth of goethite so that hematite can form competitively. In fact, an $\text{Al}/(\text{Al} + \text{Fe})$ of 0.025 was sufficient to suppress goethite completely in favour of hematite at pH 7 even at 25 °C and this effect became stronger as the pH increased from 4 to 7 (Schulze, 1982; Schwertmann et al. 2000). At 70 °C the field of hematite formation widens as [Al] in the system increases and [OH⁻] decreases (Lewis & Schwertmann, 1979 a) (Fig. 14.22).

With the exception of Mn^{2+} and Fe^{2+} , all divalent, first row transition elements investigated to date, retard the transformation of ferrihydrite and modify the composition of the final product. The retarding effect is proportional to the level of metal (M) in the M-ferrihydrite coprecipitate (Giovanoli & Cornell, 1992). The reciprocal half conversion time of ferrihydrite, coprecipitated with Ni, to better crystalline oxides decreased linearly from 8 to $3 \cdot 10^{-3} \text{ min}^{-1}$ as the Ni concentration rose from 0 to 0.016 M (Cornell et al. 1992). At $\text{M}/(\text{M} + \text{Fe}) < 0.15$ and 70 °C, Mn^{2+} produced relatively more goethite than did the control (at pH > 10), whereas Co, Ni and Zn favoured hematite indirectly by stabilizing ferrihydrite against dissolution for long enough to enable hematite to nucleate (Fig. 14.23). Cu *directly* promoted hematite and this ability may be related to the fact that Cu^{2+} exhibits the Jahn-Teller effect, i.e. it has a distorted octahedron: the four ligands in the *xy*-plane approach the central metal atom more closely than do the two on the *z*-axis. These variations in the Cu-O/OH bond lengths may facilitate adjustments in the M-O-OH distances (Cornell & Giovanoli, 1988) which, as EXAFS measurements have shown, must precede devel-

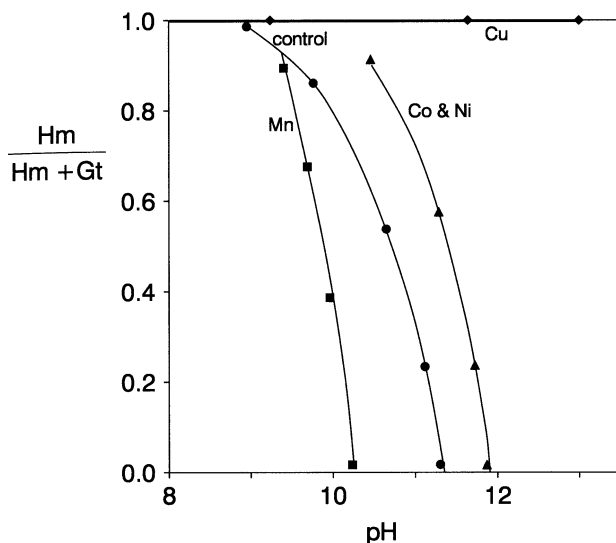


Fig. 14.23 The effect of Mn, Co, Ni and Cu on the amounts of hematite and goethite ($Hm/(Hm + Gt)$) formed from 2-line ferrihydrite at various pH and 70 °C. $M/Fe = 0.1$ (Giovanoli & Cornell, 1992; with permission).

opment of hematite in ferrihydrite (Combes et al., 1989). At 30 °C, similar levels of Cu suppressed goethite without promoting hematite – in fact the kinetics of the whole reaction were strongly retarded at this lower temperature (Inouye et al., 1972). At pH 7.5–8 and 70–90 °C, Mn and Ni at a $M/(M+Fe) = 0.011–0.063$ suppressed goethite completely in favour of hematite (Wells et al. 2001).

With $M/(Fe + M) > 0.15$, a spinel phase (MFe_2O_4) formed in all cases and when this ratio exceeded 0.33, Cu and Ni precipitated as separate phases (Tab. 14.3). Formation of a spinel phase requires a threshold level of M^{2+} in the system. It is considered that the spinel phase nucleates in the water layer adsorbed on or adjacent to, the surfaces of the ferrihydrite particles and that these nuclei grow by addition of soluble M-Fe-hydroxo complexes released by the dissolving M-ferrihydrite (Cornell & Giovanoli, 1987, 1989; Giovanoli & Cornell, 1992). Tronc et al (1992) suggested that when the Fe^{II}/Fe^{III} ratio is very low, a different mechanism operates: a mixed valence state with short-range order which displays electron hopping, forms. Electron delocalization in this phase causes local structural rearrangements and is the driving force for magnetite formation.

The M-ferrihydrite coprecipitate contains M-O/OH-Fe and M-O/OH-M as well as Fe-O/OH-Fe linkages. The transition elements stabilize ferrihydrite in the order, $Mn < Ni < Co < Cu < Zn$ (Cornell, 1988; Giovanoli & Cornell, 1992). This order does not correspond with that of the electronegativities or the crystal field stabilization energies (CFSE) of these elements, nor does it match the order of binding constants for the M-surface complexes. If Zn is omitted from the series, however, there is a reasonable cor-

Tab. 14.3 Compounds formed after 50 d, from ferrihydrite coprecipitated with different levels of divalent ions at pH 12 and 70 °C (Giovanoli & Cornell, 1992; with permission)

Ion	Ionic radius nm	Ratio $M/(Fe+M)$ added		
		0.09	0.18	0.33
		<i>mol mol⁻¹</i>		
*Mn ²⁺	0.082	Gt	Gt + Sp	Sp + Gt
*Co ²⁺	0.074	Gt	Gt + Sp	Sp
Ni ²⁺	0.069	Gt	Gt + Sp	α -3 Ni(OH) ₂ · 2H ₂ O + Sp
Cu ²⁺	0.073	Hm	Hm + Sp	Sp + CuO
Zn ²⁺	0.074	Gt + Hm	Hm + Sp	Sp

Gt: goethite; Hm: hematite; Sp: spinel

* Mn and Co are incorporated in Gt as trivalent ions (ionic radii 0.0645 and 0.061 nm, respectively).

relation between the stabilizing ability of the metal and the increasing covalency (and hence stability) of the M-O/OH bond along the series Mn to Cu. At present, there is no clear explanation as to why Zn does not fit into this series. Whether the foreign element is incorporated or only adsorbed may be relevant. For example, in spite of forming less stable surface complexes, coprecipitated Ni retarded the transformation of 2-line ferrihydrite to goethite at pH 6 and pH 11 and 70 °C more than did Pb, probably because, as shown from dissolution kinetics, Ni is incorporated into the ferrihydrite whereas Pb is not (Ford et al. 1999). Before a satisfactory hypothesis accounting for all the effects metal ions have on the stability of ferrihydrite can be developed, a detailed examination of the structure of the ferrihydrite/solution interface and the manner in which the metals are incorporated into the coprecipitate, is thus required. The matter is complicated by the poorly ordered nature of ferrihydrite.

Although titanium retards the transformation of ferrihydrite (pH 6–11), it enhances the formation of goethite over hematite (Fitzpatrick & Le Roux, 1976; Fitzpatrick et al., 1978). The opposite was found for trivalent chromium (Schwertmann et al., 1989) and vanadium (Schwertmann & Pfab, 1994); besides retarding the transformation, higher concentrations of both ions led to enhanced hematite formation.

A rare example of a cation accelerating the transformation of ferrihydrite to goethite is Fe²⁺ (Fischer, 1972) (Fig. 14.24). The rate of transformation is at a maximum at pH 6.5 which coincides with the pH of maximum Fe²⁺ adsorption by ferrihydrite (insert in Fig. 14.24); at lower pH, Fe²⁺ adsorption falls off due to the increasingly positive charge of the ferrihydrite and at higher pH, Fe²⁺ is increasingly hydroxylated and thereby deactivated. The first step in the process, adsorption of Fe²⁺, is followed by electron transfer to interfacial Fe^{III} and this electron transfer is continually repeated. The function of Fe²⁺ in promoting goethite formation can, thus, be seen in its ability to promote reductive dissolution of ferrihydrite (see Chap. 12). Higher levels of Fe²⁺ interact with ferrihydrite to form magnetite preferably at pH values > 7 (Ardizzone & Formaro, 1983; Mann et al., 1989). This may be an important route for magnetite formation in magnetotactic bacteria (see chap. 17). (For transformation of other Fe oxides into magnetite in the presence of Fe²⁺ see section 14.4.2).

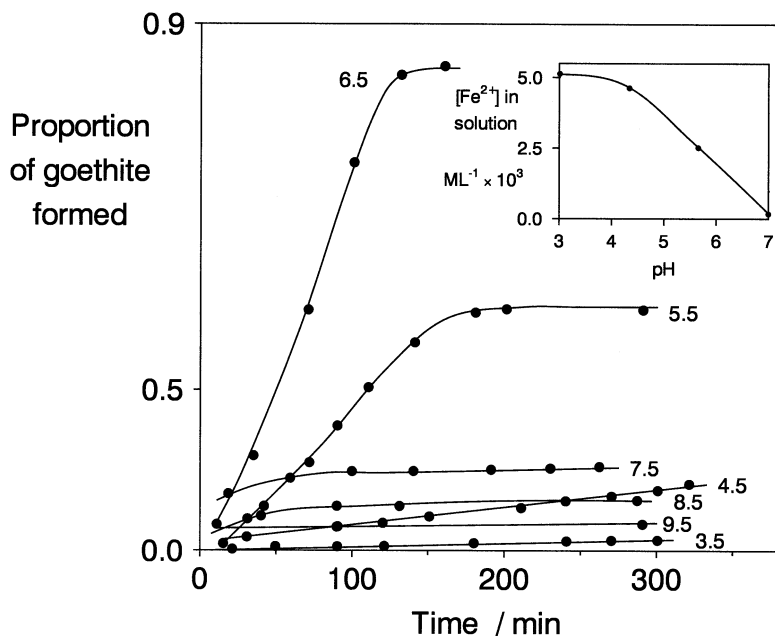


Fig. 14.24 Transformation of ferrihydrite to goethite with time at 50 °C in the presence of $5 \cdot 10^{-3} \text{ M Fe}^{2+}$ at various pHs (pH values given on the curves). Insert: Fe^{2+} concentration in solution after 30 min vs. pH (Fischer, 1972; with permission).

14.4

Oxidative and reductive transformations

14.4.1

Oxidation of magnetite to maghemite or hematite

In the dry state magnetite is readily oxidized to maghemite by air. Ultrafine crystals of magnetite change (over years) from black to the brown of maghemite even at room temperature (Murad & Schwertmann, 1993). At temperatures $> 300^\circ\text{C}$, the transformation proceeds further to hematite (see section 14.2.7).

Oxidation of magnetite under these conditions involves a topotactic reaction in which the original crystal morphology is maintained throughout (Feitknecht & Lehmann, 1959; Feitknecht, 1965; Gallagher et al., 1968). Initially a mixed phase, $\text{Fe}_{1-x}^{\text{II}}\text{Fe}_{2+x}^{\text{III}}\text{O}_{4+0.5x}$ with less Fe^{II} , more Fe^{III} and more cation vacancies than has magnetite, forms. This phase then oxidizes further (Feitknecht, 1965). During the reaction, the density of the starting material falls and the weight of the sample increases because oxygen is taken up:



No porosity develops, however, and the sample surface area does not change (Sidhu et al., 1977).

Oxidation to maghemite involves a reduction in the number of Fe atoms per unit cell of 32 oxygen ions, from 24 in magnetite to $21\frac{1}{3}$ in maghemite. The reaction proceeds by outward migration of the cations towards the surface of the crystal together with the creation of cation vacancies (Feitknecht, 1964; Gallagher et al., 1968) and the addition of oxygen atoms. At the surface the cations are oxidized and interact with adsorbed oxygen to form a rim of maghemite. The diffusion coefficient for cation migration is $1-2 \cdot 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. Substitution of $<0.01 \text{ mol mol}^{-1}$ of heavy metals (Co, Ni and Zn) reduces the cation diffusion coefficient (Sidhu et al., 1977). Activation energies for this transformation of between 83.6 kJ mol^{-1} (Sidhu et al., 1977) and 137 kJ mol^{-1} (Gillot et al., 1978) have been reported. The activation energy appears to depend on sample surface area and on whether or not there is Al substitution.

A feature of this transformation is the influence of magnetite crystal size on the nature of the reaction products (Feitknecht, 1964; Gallagher et al., 1968; Gillot et al., 1978). At 200–250 °C, crystals smaller than 300 nm transformed via the mixed phase to maghemite which in turn transformed to hematite at temperatures above 500 °C. In magnetite particles larger than 300 nm, some hematite nuclei formed even at lower temperatures and maghemite formation was bypassed. In small crystals, the diffusion pathways are short and reaction rates, therefore, fast, so that complete oxidation is achieved rapidly. In larger crystals, diffusion pathways are too long for complete transformation of magnetite to take place; for it to occur, the temperature must be raised above 500 °C. At ca. 220 °C, the outer layer of maghemite that formed initially blocked further conversion at this temperature. With somewhat higher temperatures (320 °C), structural strain arising as a result of the oxidation process caused spontaneous nucleation of hematite in the maghemite layer. Following this, the remainder of the intermediate mixed phase underlying the maghemite rim disproportionated to a mixture of magnetite and hematite, and at temperatures greater than 400 °C, the remainder of the magnetite transformed to hematite. At high enough temperatures ($>500 \text{ °C}$) macroscopic magnetite changed directly to hematite; the kinetics of this reaction followed a parabolic law.

Sidhu et al. (1981 a) compared the oxidation upon heating, of natural and synthetic magnetites. The coarse, natural magnetites were much more resistant to oxidation and higher temperatures or longer times were needed for it to take place. Hematite was the only oxidation product, which is in agreement with the results quoted above. On the other hand, the reduction in the edge length of the cubic unit cell from 0.839 to 0.834 nm indicated that at 200 °C, synthetic magnetite changed to maghemite (Sidhu et al., 1981 a) (Fig. 14..25). It was suggested that a small amount of OH in the synthetic magnetite (which is absent in natural sample) is a prerequisite for maghemite formation. Most of the trace elements (Co, Ni, Zn, Cu, Mn, Cr) were retained by the maghemite formed at 220 °C from small, synthetic, substituted magnetite crystals; the outer regions contained less of these elements indicating an outward movement of Fe during the transformation (Sidhu et al., 1980). Only a small percentage of structural Zn and Ni was ejected during conversion at 600 °C of large, natural, magnetite crystals to hematite (Sidhu et al., 1981 a). Under UHV, a magnetite film

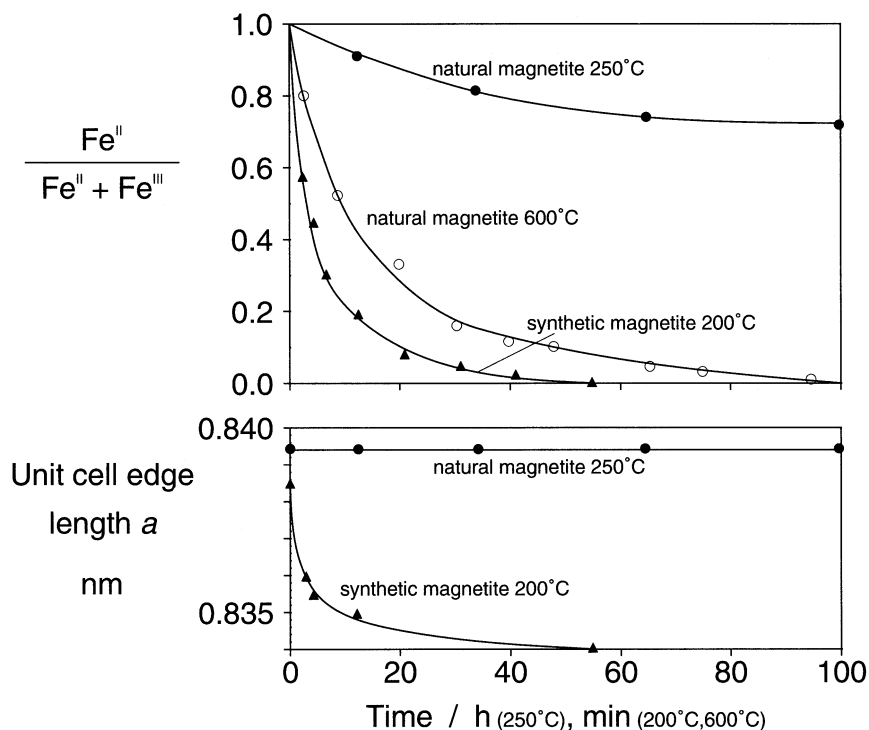


Fig. 14.25 Change in degree of oxidation and unit cell size of synthetic and natural magnetites with time of heating. (The time scale is in minutes for synthetic and in hours for natural magnetites) (Sidhu et al., 1981 a; with permission).

could be converted to hematite within 30 min by heating in 10^{-4} mbar O_2 at 727°C : the transformation was reversed by holding at this temperature in $<10^{-6}$ mbar O_2 (Ketteler et al. 2001).

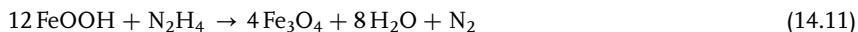
Magnetite transforms to maghemite (and thence to hematite) in water or alkali under hydrothermal conditions. Conversion to maghemite also involves outward migration of cations via cation vacancies (Swaddle & Oltmann, 1980). The hydrothermal transformation is slower than that in air at the same temperature (180°C) and it has been suggested that this is because the cation vacancies which assist cation diffusion are reduced or eliminated by the large excess of water.

In acid media (pH 2) magnetite crystals ca. 10 nm across transform topotactically to maghemite via an adsorption reaction which traps mobile electrons from the bulk material and reduces interfacial Fe^{III} ; the Fe^{II} ions that form are selectively leached into solution (Jolivet & Tronc, 1988). Electron delocalization also induces ferrihydrite in contact with small magnetite particles to transform into a spinel layer (Belleville et al., 1992).

14.4.2

Reduction of Fe^{III} oxides to magnetite

In alkaline media (pH 9–11.5) at 100 °C and in the presence of hydrazine, *akaganéite* dissolves and reprecipitates as magnetite in ca. 3 h (Blesa et al., 1986 a). The overall reaction,



incorporates a number of different steps. Neither dissolution of *akaganéite* nor growth of magnetite appears to be rate determining. The reaction is first order with respect to the concentration of hydrazine which suggests that the rate determining step is the reduction of Fe^{III} released by dissolution of *akaganéite*. The reaction rate is pH sensitive with a minimum at pH 10.4. This minimum has been attributed to the combined effects of a possible change in *akaganéite* solubility with rising pH and, more probably, to different reactivities of various soluble hydrolysed Fe^{III} species with hydrazine. Full details of the mechanism have not been established. It is suggested that it involves adsorption of Fe^{II} species on the surface of the *akaganéite* crystals thereby facilitating their dissolution (see Chap. 11 & 12). SEM examination indicated that a limited number of magnetite nuclei developed, via interaction of Fe^{II} species with surface hydroxyl groups either on the *akaganéite* surface or in the associated water layer. Seeds of goethite or hematite did not serve as a substrate for magnetite nucleation, but instead grew further in preference to magnetite which was eliminated from the system.

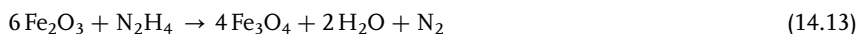
In the presence of Fe^{II} ions, *lepidocrocite* transforms into magnetite in alkaline media (Tamaura et al., 1983). The transformation which takes place at room temperature is stoichiometric, i.e.



Neutralization of H⁺ promotes the reaction and keeps the system supersaturated with respect to magnetite. The laths of *lepidocrocite* gradually transform into numerous, much smaller cubic crystals of magnetite. In the same way as with *akaganéite*, the transformation is via solution. The mechanism is thought to involve adsorption of Fe^{II} species on and interaction with, surface groups of the *lepidocrocite* to form magnetite directly (or via Fe^{II,III} hydroxo species), either on the surface or in the water layer adjacent to the surface. A similar mechanism has been proposed for formation of magnetite from *Fe(OH)₂* and from *ferrihydrite* (Schwertmann & Thalmann, 1976; Sugimoto & Matijevic, 1980; Mann et al., 1989). Soil *lepidocrocite* has also been converted to magnetite in the presence of a 0.1 M FeSO₄ solution (Schwertmann & Taylor, 1973). Two-line *ferrihydrite* in acetate- or H₂/CO₂-enriched cultures was transformed to magnetite and siderite at 45–75 °C by a thermophilic bacterium obtained from sedimentary rocks, in agreement with the Eh and pH conditions (Chuanlun et al. 1997).

Hematite transformed to magnetite under hydrothermal conditions in alkaline solution containing hydrazine¹⁾ (Sapieszko & Matijevic, 1980), i.e.

1) Hydrazine is used as an anti-oxidant in boilers.



The spherical or disk-like particles of hematite dissolved and large, octahedral crystals of magnetite precipitated. The dissolution process involved electron transfer between hydrazine and the Fe^{III} of the hematite and was promoted by complexing agents such as TEA.

14.4.3

Reduction of iron ores to iron

In the blast furnace, high temperature interaction of hematitic ores with reducing gases – a CO/CO_2 mixture – produces metallic iron via a series of intermediate oxides, i.e. hematite $\rightarrow$ magnetite $\rightarrow$ wüstite $\rightarrow$ iron. The rate determining step of the overall reaction is considered to be the reduction of wüstite (Bradshaw, 1970). Full details of all the processes involved are given by Bogdandy and Engell (1971).

Laboratory investigations of gaseous reduction of iron ores have been prompted by the importance of these reactions in the blast furnace. The ultimate aim has been to understand the processes involved and in particular, to determine the conditions under which rapid reduction occurs, so as to improve the reducibility of the ore. Such studies have been carried out over a range of temperatures, with CO/CO_2 or $\text{H}_2/\text{H}_2\text{O}$ gas mixtures of varying compositions and either on the ores themselves or on synthetic single crystals of Fe^{III} oxides. As the reaction mechanisms which operate are extremely sensitive to these conditions and also to engineering parameters, it is not surprising that there are often discrepancies between the kinetic data of various investigators (Bradshaw, 1970). There is better agreement between the different morphological studies.

This section makes no attempt to cover all the many studies on this field; rather attention is drawn to certain well established features of the hematite to magnetite transformation. Investigations involving sized (45–63 μm) particles of both ore hematite and synthetic crystals (50–800 μm) showed fairly good agreement for both the kinetic and the morphological data (Hayes & Grieveson, 1981; El-Tabirou et al., 1988). The partly reacted crystals were examined by optical and electron microscopy and the kinetics of the reaction were followed by thermogravimetric and gravimetric methods. A feature of this reaction is that, depending on the reaction conditions, the magnetite produced may be either lamellar or porous (Swann & Tighe, 1977). Magnetite grows as lamellae into the hematite matrix along specific crystal directions and is often accompanied by fissuring of hematite. The transition from lamellar type magnetite to a porous shell enclosing the hematite is a function of both the temperature of the reaction and the CO concentration in the reducing gas. Lamellar magnetite is favoured by higher temperatures and lower CO concentrations (Swann & Tighe, 1977; Hayes & Grieveson, 1981; El-Tabirou et al., 1988).

Under conditions leading to a porous shell of magnetite, the kinetic curve displayed an induction period corresponding to formation of nuclei and the subsequent reaction followed the cube root law. Diffusion of the reducing gas to the reactant/product interface took place readily with a porous product. Whether chemical or diffusion control predominated depended on reaction conditions. With small crystals

or at temperatures of ca. 500 °C, chemical control governed the reaction, whereas mixed chemical and diffusion control operated with large crystals and/or temperatures in excess of 800 °C (El-Tabirou et al., 1988). When the magnetite is lamellar (non-porous) and a physical barrier separates the reducing gas and the hematite, the reaction involves diffusion of iron atoms through the product.

The reduction of hematite with H_2 at 387–610 °C has been followed *in situ* using TEM and an environmental cell (Rau et al., 1987). The reduction reaction started at nucleation sites on the edge of the sample and as the reaction proceeded, a particle showed four reaction zones consisting of unreacted hematite, lamellar magnetite, porous magnetite and finally porous iron (the temperature was too low for wüstite). The rate controlling step was considered to be the reduction of magnetite to iron. During the reduction of hematite to magnetite there is an overall increase in volume due to dilation parallel to the c axis of hematite: the dilation behaviour is dependent upon the reduction temperature (Husslage et al. 1999).

Wüstite is reduced to iron at temperatures greater than 700 °C in both CO/CO_2 and H_2/H_2O mixtures. SEM examination of partly reduced crystals showed that the product could be porous iron, dense iron overlying porous wüstite or dense iron and wüstite together depending on the reaction conditions and their effect on the relative rates of the chemical and the diffusion processes (St. John et al., 1984, 1984 a).

14.5

Interaction of iron oxides with other metal oxides and carbonates

Although these interactions cannot be classed as interconversions between iron oxides, they are briefly mentioned here because they play an important part in blast furnace reactions and in the production of ferrites (Bogdandy & Engell, 1971; MacKenzie, 1982). A range of ferrites is produced for use in magnetic and electronic devices and also for production of cement refractories. Cu ferrites are found (as unwanted products) in slags from Cu ores contaminated with pyrites and in Portland cement clinker. Interaction between the iron oxides and the metal oxide or carbonate is accomplished by mixing the two compounds and heating them at 600–1300 °C, usually in air, but sometimes in an inert or reducing atmosphere (MacKenzie, 1982). Basically, the reaction involves counter diffusion of the metal ions. Each reaction may, however, have its own features. In the ZnO/Fe_2O_3 system, for example, ZnO evaporates and some Zn is redeposited on the hematite and diffuses inwards. A large excess of hematite inhibits the reaction, possibly by blocking nucleation of the ferrite phase (Feltz & Martin, 1987). Formation of barium hexaferrite from barium carbonate and hematite involves two main steps with a number of solid state reactions being involved; this complicated process has been investigated intensively (Steier et al., 1999, and references therein). Where several different reaction products are possible, they are produced by varying the reaction conditions and the proportions of each compound in the mixture.

15

Rocks and ores

15.1

Introduction

The crust of the earth, the *lithosphere*, consists of rocks. The geological definition of rock is “any naturally formed, consolidated or unconsolidated material (excluding soils, see Chap. 16) having some degree of mineralogical and chemical constancy” (Gary et al., 1973). Rocks are the primary sources of and supply most of the elements cycled through the earth's surface ecosystems including man. Of these elements, iron with an average concentration of 51 g kg^{-1} is the third most abundant cationic element after Si (269 g kg^{-1}) and Al (81 g kg^{-1}). There is, therefore, hardly any rock completely free from Fe and whenever and wherever rocks weather to form a soil, iron is channelled into the global cycle of the elements.

By convention, rocks are divided into three groups: magmatic (volcanic or extrusive and plutonic or intrusive), metamorphic and sedimentary rocks. Iron ores being the source of iron as a metal, are also rocks and are common in all three groups. Most rocks contain iron oxide minerals of varying nature and abundance. This chapter collects information about their occurrence (Tab. 15.1), properties and formation.

Iron ore production for the iron and steel industry accounts for more than 99% of the total iron mined. At present, the largest iron ore mine in the world is Mount Whaleback in the Pilbara district of Western Australia. Most of the ore there is in the form of banded iron formations (BIF) and consists of hematite and goethite.

15.2

Magmatic and metamorphic rocks and ores

The information in this section mainly follows the reviews of Frost and Lindsley (1991) and Frost (1991). The only Fe oxides of importance in *magmatic* rocks are Fe-Ti oxides, viz. titanomagnetites and ilmenites, and to a lesser extent, hematite. The term *titanomagnetite* in its common usage embraces both the true titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) and their oxidized equivalents (titanomaghemites). They vary greatly in composition with x ranging between 0 (magnetite) and 0.8; the end member, ulvos-

Tab. 15.1 Dominant occurrences of the different Fe oxides in geological formations.

Goethite	Rocks: Ubiquitous in small concentrations in consolidated and unconsolidated rocks of any age but to a lesser extent in Palaeozoic and older rocks Ores: minette, oolitic rocks, laterite crusts, Trümmererze, bog ores
Lepidocrocite	Bands in unconsolidated Quaternary rocks
Akaganéite	Hot brines
Schwertmannite	Acid pyrite-weathering waters, acid mine waters
Ferrihydrite	Bands in unconsolidated Quaternary rocks, ferriferrous springs, acid mine water deposits, bog ores, lake waters
Hematite	Red beds, banded iron formations, laterite crusts, hot brines
Magnetite/ maghemite	Ubiquitous in rocks

pinel, Fe_2TiO_4 ($x = 1$) is rare. Fe can be replaced by many other cations, besides Ti, particularly by Mg, Mn, Ni, Zn, Al, Cr and V (see Chap. 3).

The abundance of titanomagnetites in magmatic rocks ranges between approximately 10 and 70 g kg⁻¹ (Wedepohl, 1969) (Tab. 15.2). Basalts are highest in titanomagnetites and as the rock becomes less mafic, the concentration decreases. Trachites, liparites and phonolites have much lower concentrations, whereas rhyolites are intermediate. Similar trends in composition can be seen in intrusive rocks where gabbros have higher concentrations of magnetites than do granites, although the general level is lower than in volcanic rocks.

Ilmenites are also widespread in magmatic rocks with a concentration range similar to that of magnetite (Tab. 15.2). Whereas titanomagnetites cover a wide range of compositions (see above), ilmenites ($\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$) are much closer to the ideal composition ($0.75 < x < 0.95$). The solid solutions are called titanohematites or hemo-ilmenites. Ilmenites in acid rocks are usually more oxidized (higher $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratio) than those in basic rocks (Fig. 15.1).

The composition of titanomagnetites in various magmatic rocks is shown in terms of Fe^{II} , Fe^{III} and Ti^{IV} in Figure 15.1. Factors which determine this are the composition of the melt, the rate of cooling and the oxygen fugacity. Phases close to ulvospinel ($x = 0.8$) occur in highly reduced lavas, whereas silicic igneous melts, because of their higher oxygen fugacity, lead to Fe-Ti oxides higher in Fe^{III} and lower in Ti. For example, titanomagnetites from tholeiitic basalts tend to be higher in Ti than those from andesitic and dacitic lavas and also from alkalic basalts. Titanomagnetites in rhyolites associated with fayalite ($\text{Fe}_2^{\text{II}}\text{SiO}_4$) contain more Ti than those associated with biotite and hornblende.

As they have high melting points, titanomagnetites and ilmenites crystallize at ca. 1300 °C, i.e. early during the crystallization of rocks. Their crystal size depends on the cooling rate: the faster the cooling, the smaller the crystals. Crystals 1 µm in size or smaller occur in volcanic rocks, whereas intrusive rocks, which cool down at a lower rate, contain crystals up to 100 µm. Because, however, compositional gaps exist

Tab. 15.2 Average magnetite and ilmenite content (g kg^{-1}) of magmatic rocks (Data from Wedepohl, 1969)

	<i>Granitic rocks</i> ¹⁾	<i>Intermediate rocks</i> ²⁾	<i>Gabbroic-basaltic rocks</i> ³⁾	<i>Peridotitic-anorthositic rocks</i> ⁴⁾	<i>Alkalic rocks</i> ⁵⁾
Magnetite	12–33	33–56	37–46	37; 12	33–74
Ilmenite	3–14	12–29	24–50	15; 9	12–62

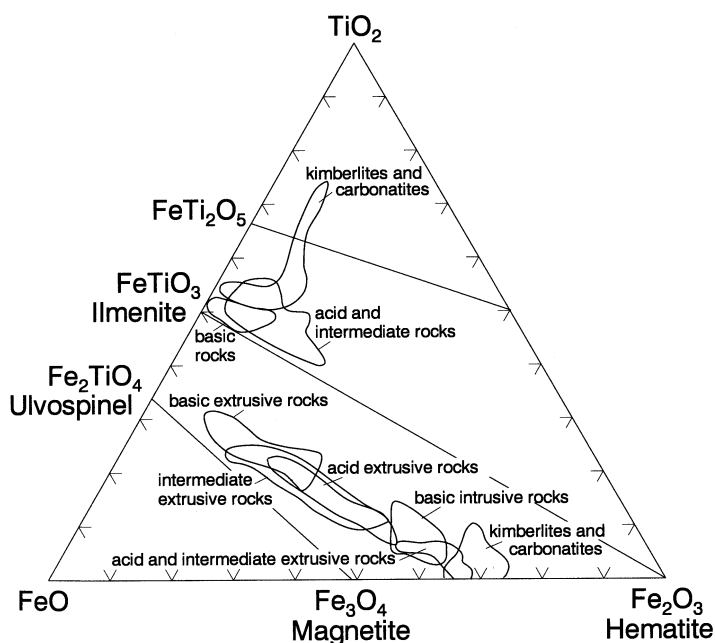
1) granites, rhyolites, quartz-monzonites, quartz-latites, quartz-diorites, dacites

2) syenites, trachites, monzonites, latites, monzodiorites, diorites, andesites

3) gabbros, tholeiitic basalts, alkali olivine basalts

4) peridotites, anorthosites

5) syenites, phonolites, essexites, tephrites, ijolites, nephelinites, leucitites, melilitites

**Fig. 15.1** The composition of titanomagnetites and ilmenites in various igneous rocks (Piper, 1987, with permission).

at lower temperature, titanomagnetites decompose by exsolution into stable phases on cooling. The slower the cooling the more pronounced is the exsolution. Thereby zonal arrangements of Ti-rich and Ti-poor phases or even of their end members (ilmenite, hematite) form, thus leading to composite grains. At the same time, oxidation may take place (oxy-exsolution). For example, at 750°C and an oxygen fugacity of 10^{-6} – 10^{-7} MPa, ilmenite zones richer in Ti and titanomagnetites richer in Fe^{III} than the initially formed oxides, may develop. Ti-hematite may even exsolve to rutile

(TiO_2) and hematite, or sometimes to pseudo-brookite (Fe_2TiO_5). Unmixing may, however, be sluggish, so that part of the mixed phase is preserved at lower temperature. This is more the case for titanomagnetites than for ilmenites because the former exsolve only below 600°C where the exsolution is very slow. Low-temperature oxidation of titanomagnetites leads to *titanomaghemites*. Titanomaghemites with a composition of $x \sim 0.6$ formed from titanomagnetite are among the most abundant Fe-Ti oxides in weathered oceanic pillow basalts. They also form during terrestrial weathering and occur in soils (see Chap. 16).

In summary, the composition of Fe-Ti oxides in magmatic rocks provides the petrologist with important information about the oxygen fugacity and temperature and also the silicon activity of the magma. It also has a strong effect on the magnetic properties of these phases (see Chap. 6 & 7).

Magnetite, ilmenite and hematite are also the main Fe-(Ti) oxides in *metamorphic* rocks (Frost, 1991). Rock types containing magnetite are metaperidotites, metabasites, iron-formations, gneisses and some metapelites. Magnetite alone is usually found in metamorphic rocks, except in high-grade metamorphites where it occurs together with ilmenite and contains some Ti. Ilmenite is found in metapelitic and metabasic rocks and may also occur in metaperidotites; it is rarely found in metamorphosed carbonates. Hematite is found in metamorphosed iron-formations, metabasites with low grade metamorphism, aerobic clay rocks and metamorphosed manganese rocks. It often contains Ti (titanohematite). As in magmatic rocks, the Fe-Ti oxides may be used as a geothermometer.

An enormous amount of literature about titanomagnetites and other magnetic minerals exists because these minerals are the main carriers of rock magnetism and therefore form the basis of the field of *palaeomagnetism*. Palaeomagnetism provides some of the quantitative data about the past location and movements of continents and oceanic plates. Thereby, it has added substantially to the plate tectonic theory. It also contributed to the refinement of stratigraphic correlation of rocks. Thus, palaeomagnetism has become an important instrument in the field of tectonics and geochronology (Butler, 1992). It has also become a useful tool in archaeological (archaeomagnetism) and environmental research. (For details the reader is referred to various comprehensive treatments, e.g. Collinson, 1983; Piper, 1987; Soffel, 1991; Butler, 1992).

15.3

Sediments and sedimentary rocks

The Fe content of sediments varies greatly with the type of rock (Wedepohl, 1969a). Sandstones contain ca. 10 g kg^{-1} Fe, claystones ca. 50 g kg^{-1} and carbonatic rocks ca. 4 g kg^{-1} Fe. In recent deep sea sediments Fe contents are low in carbonates (9 g kg^{-1}), but high in clays (65 g kg^{-1}). Sedimentary iron minerals belong to the groups of oxides, carbonates, clay silicates and sulphides. In addition, Fe is a common impurity in other sedimentary minerals.

Sediments contain detrital and neoformed Fe oxides. Among the detrital oxides are those which survived weathering due to their high stability in surface environ-

ments. Titanomagnetites and ilmenite are the two most important ones. Higher concentrations of these minerals (i.e. high enough to be worth mining) may occur in sandy sediments such as beach sands. As in magmatic and metamorphic rocks, titanomagnetites are responsible for most of the magnetism of sediments which is similarly useful in palaeomagnetic studies.

Our knowledge about the forms and genesis of neoformed Fe^{III} oxides in sediments and sedimentary rocks is still rather limited because the low concentrations and poor crystallinity of these oxides hinder their identification and description. Two groups of Fe-containing sediments, whose Fe oxides have, however, attracted more interest than usual, are red beds and sedimentary iron ores (Füchtbauer, 1988).

15.3.1

Red beds

Red beds are continental or marine sedimentary rocks with an eye-catching red colour which has been responsible for the interest in them. They are widespread all over the world and belong mainly to the Late Palaeozoic, Early Mesozoic, and Late Cenozoic periods.

In terms of the Munsell hue (see Chap 6) the colour of red beds varies usually between 5YR-2.5YR (reddish-brown to red), but may also extend into 10RP-7.5RP (red-purple). A more detailed colour measurement using the CIE $L^*a^*b^*$ system places the red beds within a space encircled by a range of synthetic hematites of different crystal sizes, as seen in Figure 15.2. This makes it likely that the colour of red beds is determined by hematite.

Indeed, hematite has often been identified in red beds (Heim, 1970; Wilson, 1971; Van Houten, 1973; Walker, 1976; Mader, 1982, 1983, 1983a, Kipli et al. 2000). Under a petrographic microscope it appears in different forms. In the Moenkopi red beds (Triassic) of the Colorado Plateau, for example, Walker et al. (1981) distinguished six forms ranging in particle size from an “ultrafine” red pigment (single crystals not visible at 50,000 x magnification) to coarse (2–40 μm), specular hematite (Fig. 15.3). Old Red Sandstone (Devonian) sediments widespread in Scotland contain hematite as the main Fe oxide; the large size (several μm) and euhedral shape of the crystals indicate diagenetic formation (Wilson, 1971). Silurian and Devonian red claystones (2.5YR) from the East Baltic contain, on average, 1.7% hematite and 0.6% goethite, whereas the yellow interlayers have between 1.6 and 12.5% goethite (by XRD). Metabentonites formed from volcanic ash in the same area were purple red (7.5–10RP), although they contained only 2.7% hematite on average. All these Fe oxides were considered authigenic (Kipli et al. 2000). Starlike twins of goethite were also found. In Lower Triassic sandstones from the Western Eifel mountains (Germany), Mader (1982) distinguished two genetic types of hematite, viz. primary, detrital hematite occurring as coatings and as impregnations of rock fragments, and secondary, authigenic and idiomorphic hematite crystals several μm in size and arranged in aggregates. He suggested that secondary hematite had formed from the primary material by Ostwald ripening or as pseudomorphs of goethite, biotite, or pyrite. Authigenic hematite with various crystal shapes, formed from magnetite, biotite and ilmenite

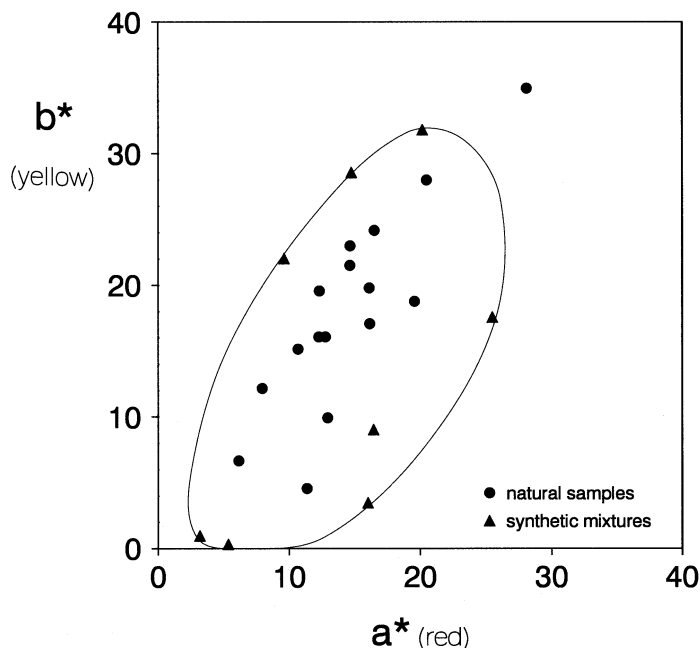


Fig. 15.2 Position of 16 red beds in the CIE $L^*a^*b^*$ colour space as compared with 8 synthetic hematites of different colour between yellow-red and purple in a 3% hematite – 97% kaolinite mixture (Torrent & Schwertmann, 1987, with permission).

by oxidation, was also found in onshore samples of red sandstone from the Triassic Skagerak Formation in Denmark (Weibel, 1998) and a pseudomorphous transformation of goethite into hematite was observed as the temperature increased from 47 °C to >105 °C with increasing burial depth (550 m → 2500 m) (Weibel and Grobety, 1999). This transformation was postulated by Berner (1969) on the basis of stability experiments. The larger, idiomorphic hematite crystals were concentrated in the pore space of the purple layers and had caused cementation of the coarser mineral grains. Hematite crystals of similar size (2–5 μm) were also observed by Heim (1970) in Lower Triassic sandstones in Germany. The presence of hematite in Triassic sediments in the Cordilleras Beticas in Southern Spain was confirmed by diffuse reflectance spectroscopy (Barrón & Montealegre, 1986). Hematite crystals in 17 samples of Triassic reddish brown shales in Maryland (USA) had an average MCL_{110} of 77 nm and an $\text{Al}/(\text{Fe} + \text{Al})$ ratio as low as 0.002–0.065 (Elless & Rabenhorst, 1994).

It has been suggested that an increase in the grain size of hematite may change the colour of hematite and hence that of the sediment from red to purple in agreement with the changes of synthetic hematite from red to purple as the crystals become larger (see Chap. 6). However, for 16 samples of red beds of Permian, Triassic and Tertiary age, including some purple saprolites from basalts and shale, no relationship between the size of hematite crystals and the degree of purple was found

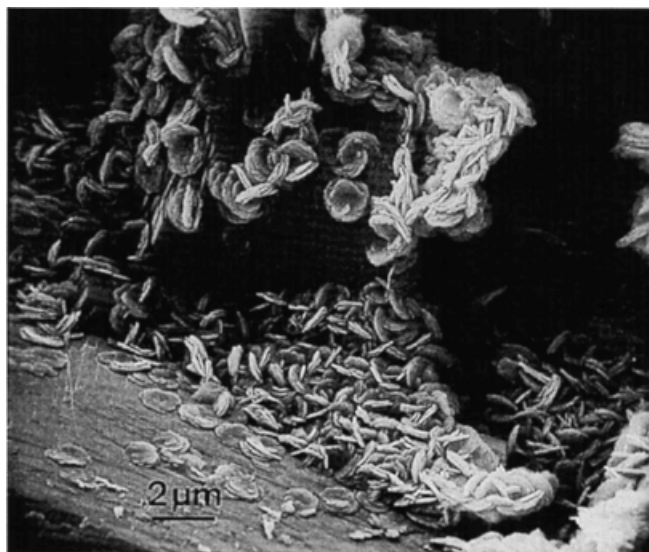


Fig. 15.3 Aggregates of authigenic hematite rosettes from a Triassic sandstone of the Moenkopi Formation near Gateway, Colorado, USA (Walker et al., 1981, with permission; courtesy T. R. Walker).

(Torrent & Schwertmann, 1987). It was, therefore, hypothesized that oriented aggregates of platy hematite crystals may have optical properties similar to larger single crystals and, thus, are responsible for the purple colour. This is supported by the fact that aggregate destruction by grinding, changes the colour from purple to red and yellowish-red. Turner and Archer (1977) have also observed oriented aggregates of platy hematite crystals which had grown epitaxially on a decomposing biotite in the Devonian red beds of Scotland.

Whether the hematite of the red beds is detrital or authigenic is important for the understanding of their genesis as a whole (for a detailed discussion see Blodgett et al., 1993). It was suggested that detrital hematite originated from eroded red soils (paleosols), i.e. as a result of terrestrial weathering. Conditions proposed for the formation of these continental sediments and, thus, for the neoformation of hematite, were a semi-arid climate (Walker, 1967, 1967a) with wet-dry cycles and a low-carbon environment, both favouring the formation of hematite via ferrihydrite (see Chap. 14). This mechanism requires the (re-)mobilization of Fe during diagenesis. Interbedding of red beds with grey or green layers indicates that such remobilization of Fe from Fe^{III} oxides through reductive dissolution by organic compounds has occurred, thereby supplying Fe for authigenic hematite formation. The remaining grey-green colours are those of the matrix, e.g. clay minerals. Bleached, reduced channels, probably of biogenic origin, have been described for the Lower Permian red beds near Baden-Baden, Germany (Suttor et al., 1988).

15.3.2

Sedimentary iron ores

Sedimentary iron ores worth mining comprise about 80% of the world's Fe-ore production and ca 90% of the world's reserves. To be of value, ores should contain at least $0.6 \text{ g g}^{-1}\text{Fe}$, preferably in the form of Fe oxides. Because hematite and magnetite contain more Fe per unit weight than goethite, ores in which the two former oxides predominate, are preferred. Table 15.3 summarizes the main characteristics of sedimentary iron ores.

Two groups of sedimentary iron ores, traditionally termed iron formations and iron stones (oolithic, Minette type) are usually distinguished. The *banded iron formations* (BIF) or *itabirites* are Precambrian, thin-bedded or laminated chemical sediments, consisting of millimeter layers of hematite or magnetite, interbedded with quartz or chert (for a review, see Trendall & Morris, 1983). Typically, they were formed in almost all of the Precambrian massifs around the world. After sedimentation, they were influenced more or less by metamorphic processes, which have led to a crystal augmentation of hematite (specular hematite) and quartz formation from chert. Hematite-quartz ooids, siderite, greenalite, and pyrite also occur (Maynard, 1983). With regard to the genesis of the BIF, it is assumed that hypogene solutions of Si and Fe with organic matter were supplied to a shelf zone, lagoons or lakes in

Tab. 15.3 Types of sedimentary iron ores (modified from Füchtbauer, 1988; with permission)

<i>Genetic type</i>	<i>Fe source</i>	<i>Texture</i>	<i>Main minerals</i> ¹⁾	<i>Geological environment</i>	<i>Type name</i>
Hydrothermal-sedimentary	hypogene	banded	Mt, Hm	Greenstone belts banded iron formations	Algona
"	"	layered clastic	Hm	Eugeosyncline ²⁾ Phanerozoikum	Lahn-Dill
Marine-sedimentary	"	banded	Mt, Hm	Miogeosyncline Lower Proterozoicum	Superior
"	supergene detrital	oolithic	Hm, Gt, Ch	shallow shelf	Clinton Lothringen (Minette) Salzgitter Peine-Ilse
"	"	sands	Mt, Im	littoral	
Terrestrial-sedimentary	"	massive, earthy	Gt	limnic	Amberg
Metasomatic	mesogene	massive	Sd, Hm, Mt	variable	Marquesado
Terrestrial-pedogenic	supergene	massive vesicular pisolithic	Gt, Hm, Fh	soils	Laterite Bog iron Ferricrete

1) Mt magnetite, Hm hematite, Gt goethite, Ch chamosite, Sd siderite, Im ilmenite, Fh ferrihydrite

2) A geosyncline in which volcanism is associated with clastic sedimentation

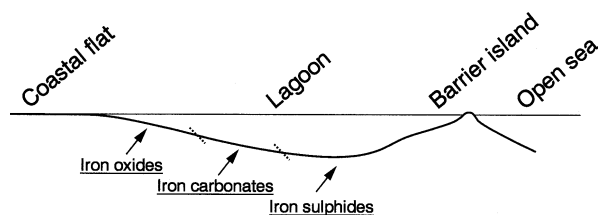


Fig. 15.4 The position of Fe oxides in a sequence of Fe minerals deposited in a lagoon environment (Reprinted with permission of *Economic Geology*, v. 78:8, p. 1670, Fig. 9, Torrez-Ruiz, J., 1983).

which, depending on the redox potential and the composition of the aqueous phase, siderite, hematite, magnetite, Fe^{II} silicates (e.g. greenalite, $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and minnesotaite, $(\text{Fe,Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), pyrite and chert were formed by seasonal precipitation (Ewers, 1983). As shown in Figure 15.4, a regular sequence of these phases can be observed over an increasing distance out from the coast, i.e. with increasing water depth. Their formation can be derived at least in part, from stability diagrams (see Chap. 8), taking pH, Eh and the activities of all dissolved species into account. Primary solid compounds, such as chert and ferrihydrite, were the metastable phases. Ferrihydrite will adsorb silicate and after its conversion to hematite by diagenesis and metamorphism, will release the Si, which precipitates as a separate phase, viz. chert and finally quartz (Harder, 1963). Perry et al. (1973) suggested that magnetite in BIF's is of biogenic origin and formed in a similar way to that in magnetic bacteria (see Chap. 17). Biogenic formation was recently proposed also for the hematite in such ores (Brown et al. 1998). Post-sedimentary processes may have led to formation of concentrated hematite layers from magnetite together with leaching of chert.

Another type of economically important Fe ore occurs in so-called *skarns*. Skarn is an old Swedish name for a gangue formation from the Archean age produced by metasomatic replacement of carbonate rocks by solutions. If rich in Fe, these solutions led to the precipitation of Fe ores containing hematite and magnetite as the main Fe oxides.

Hematitic iron ores of hydrothermal-sedimentary origin and Palaeozoic in age, are those of the *Lahn-Dill-type* in West and Central Europe (Harder, 1964). Hydrothermal solutions associated with submarine volcanic activities have transported Fe (as FeCl_3) into a marine environment, where after hydrolysis, hematite was formed (via ferrihydrite) at the margin of the basin, whereas siderite (after reduction) was formed in its centre. These ores are – in contrast to true sedimentary ores – low in Al, Ti and trace elements, which betrays their volcanic origin.

The second group of Fe ores, the *iron stones*, are Fe-rich, hard sedimentary rocks of exclusively supergene origin. They are from the Phanerozoic era and cover the time span between the Ordovician and Tertiary eras. At present, the economic value of these ores is low. Representatives of this group are the marine, fluvial or even terrestrial formations of the *Lothringen* (Minette) and *Clinton* (Eastern USA) type. The deposits of the Alsace/Lorraine region (France) were among the causes of the incessant

wars fought over these territories. The ores usually contain $<0.5 \text{ g g}^{-1} \text{ Fe}$, $>10 \text{ g kg}^{-1} \text{ P}$ and $>20 \text{ g kg}^{-1} \text{ Al}$, and their main minerals are goethite, hematite, siderite, berthierine and chamosite; magnetite is rare (Böhm, 1928; Correns & v. Engelhardt, 1941; Harder, 1951; Hegemann & Fröhlich, 1962; Siehl & Thein, 1978). Their Fe content may originate from terrestrial weathering products rich in Fe^{III} oxides (Gehring & Karthein, 1990; Schwarz & Germann, 1993), for example lateritic ferricretes. These were eroded into the sea and finally transformed by reduction/reoxidation into Fe minerals. Goethite in iron stones may have formed primarily in oxygenated coastal zones. Formation may also be secondary, resulting from oxidation of siderite or other Fe^{II} minerals.

Often iron stones have an oolitic texture, i.e. they consist of perfectly rounded bodies, the so-called *ooids*. Iron oxide ooids are mm to cm in size, hardened and showing concentric Fe accumulations (Plate 15.I), which suggest cyclic precipitation of the Fe oxide. Chemical point analysis by the electron microprobe indicates enrichment of Ti, P and V in the Fe oxides, whereas Si and Al concentrations are very low (Fig. 15.5). The mode of Fe ooid formation and in particular the need for some mechanical action to produce the perfect rounding has been a matter for discussion for a long time. In principle, both terrestrial and marine formation is possible and it

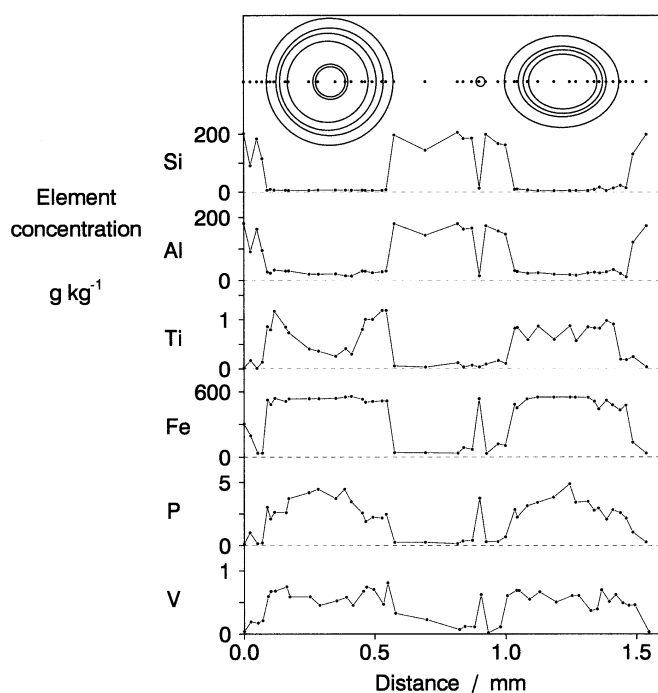


Fig. 15.5 Element distribution across two Fe oxide ooids. The position of the two ooids is also indicated (Schwarz, 1992; with permission).

seems that the spherical shape does not necessarily require mechanical movement or abrasion. It does require, however, mobile Fe^{2+} ions as an Fe source. The accumulation of Fe as Fe^{III} oxide, often occurring around a detrital core, is driven by local gradients in the redox potential, which is low in the matrix supplying Fe^{II} and locally higher (possibly due to better aeration through larger pores) where the Fe^{III} oxides form. This process of concentric precipitation may take place under terrestrial (e.g. in soils), limnic and marine conditions. In other words, detrital Fe^{III} oxides, e.g. from degrading laterites in the higher parts of the landscape, are mechanically transported into lower lying, wet areas (flood plains, coastal regions) where the Fe is reductively mobilized (see Chap. 16) and reprecipitated as ooids.

Foreign elements in the ooids may reflect the growth environment. Marine ooids may be higher in Ca, P (in the form of apatite) (Gehring, 1985), Mn, Co and Ni, than terrestrial ones. Trace elements in a reduced state, for example V^{III} and Cr^{III} , incorporated in the structure of the Fe oxides may reflect an anaerobic environment. The high pH and the low Al concentration in sea water has led to low Al substitution in goethite compared to higher levels of substitution under the terrestrial conditions under which the Fe oxides were originally formed (Correns & v. Engelhardt, 1941; Schwarz, 1992). Thus, the ooids are, in principle, not different from other widespread spherical Fe oxide concentrations such as nodules, concretions, pisoids, or geodes in sediments, soils and lakes. The palaeoenvironment of iron stone formation is, therefore, considered to be similar to that of a common surface environment. Using the oxygen isotope ratio $\delta^{18}\text{O}$ of goethite and apatite from an Upper Ordovician iron stone (440 Ma) in Wisconsin, Yapp (1993) identified meteoric water ($\delta^{18}\text{O} = 7.3\text{‰}$) at a temperature of 23°C which, in agreement with fossil marine invertebrates, points to a tropical climate with monsoonal rain.

Erosional transport of iron stones may have led to a mechanical concentration of these spherical bodies in alluvial sediments or in marine depressions and caused their breakdown (*Trümmererze*). These deposits may be recemented by Fe oxides, predominantly goethite, formed *in situ* in the interstices.

The purely sedimentary ores containing in sequence, Fe oxides, Fe carbonate and Fe sulphides may be modified by metamorphism. One example is the Marquesado deposit in Spain, in which alpine metamorphism has led to recrystallization of siderite (siderite marble), magnetite and (specular) hematite and to martite formation (Torrez-Ruiz, 1983). Iron stones may also be altered when they crop out at the surface. Pyrite (Plate 15.II) and siderite, but also biotite (see Plate 16.IV) are particularly vulnerable to weathering under atmospheric conditions (Postma, 1983; Schwertmann et al., 1995 b). The oxidation of the released Fe will preferentially form goethite. Magnetite is more stable, but again, not in equilibrium with the atmosphere and will also oxidize to pure Fe^{III} oxides such as maghemite, goethite or hematite. Even specular hematite may transform to goethite in an aqueous system viz. via a dissolution/precipitation mechanism; not by hydroxylation (see Chap. 14).

Oxidized upper zones of Fe-rich rocks with high concentrations of Fe oxides are found in pyritic (gossan) and ultrabasic rocks. These rocks are often the subject of exploration owing to their content of such non-ferrous metals as Cu, Co, Ni and Zn. These metals are intimately associated with the iron oxides, mainly goethite and he-

matite, possibly by replacement of Fe in the structure. The Fe-oxides in such ores have been characterized in gossans (e.g. de Oliveira et al. 1996), and in the upper oxidized zones of nickeliferous, ultrabasic rocks (peridotites, dunites) (e.g. Schellmann, 1983; Schwertmann & Latham, 1986).

15.3.3

Other sediments

Deep sea sediments may contain magnetite which may be not only of detrital origin, but may also contain a contribution from former magnetotactic bacteria. Petersen et al. (1986) have identified single-domain, magnetite crystals in Eocene to Quaternary sediments from the South Atlantic, which are very similar to biomagnetite in recent marine bacteria (see Chap. 17).

Unconsolidated coarse-grained sediments (sands, gravel) often contain yellow or red bands a few to several tens of cm thick (Plate 15.III). The Fe^{III} oxide content of these bands is high relative to the rest of the sediment and the oxides may cement the mineral grains. Often, these bands are associated with black ones rich in Mn oxides (e.g. birnessite, vernadite) which may contain some Fe, whereas the Fe bands themselves are almost free from Mn. Such bands occur widely in non- or weakly consolidated, Tertiary and Pleistocene sediments, but also in older sandstones. The former are interpreted as the markings of former ground water surfaces. These bands were fossilized when the ground water level was lowered by further incision by streams. Such bands have present-day equivalents in groundwater soils (gleys), where they mark the zone of annual ground water fluctuations and Fe oxide formation (see Chap. 16). Typically, the bands follow textural discontinuities, even if the latter are not horizontal. It is therefore suggested (Schwertmann, 1959b; Koljonen et al., 1976; Schwarz, 1992) that textural discontinuities induce short-range changes in the redox potential (Eh) which is low in the denser, finer sediment and high in the coarse sediment. Fe^{2+} is oxidized when it reaches the Eh jump and iron is immobilized as Fe^{III} oxide (Fig. 15.6).

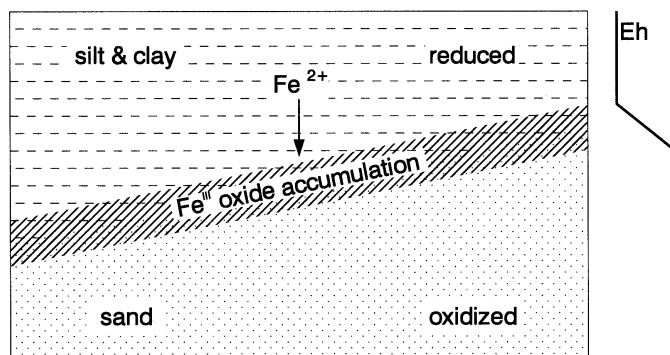


Fig. 15.6 Schematic representation of iron oxide formation at a textural (= Eh) discontinuity in unconsolidated clastic sediments.

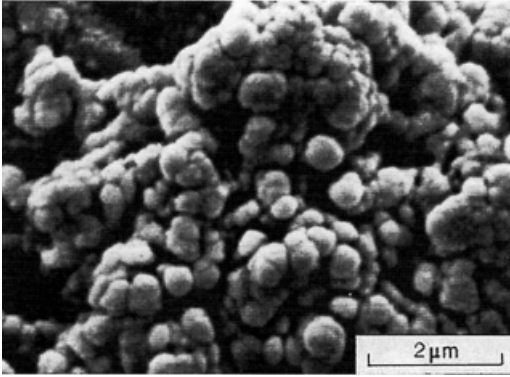


Fig. 15.7 Globular goethite aggregates on quartz grains in a 20000 year old Quarternary sand deposit at Karup, Jutland, Denmark (Postma & Brockenhuus-Schack, 1987; with permission).

A few studies of the Fe oxide minerals in such Fe oxide-rich bands are available. In temperate zones, goethite was found to be the dominant and ubiquitous Fe^{III} oxide, although lepidocrocite and ferrihydrite were also detected (Schwertmann, 1959b; Koljonen et al., 1976; Carlson & Schwertmann, 1980; Van Ranst & De Coninck, 1982; Bergseth, 1983; Dill, 1985; Hus & Stiers, 1987; Barral Silva & Guitian Ojea, 1991). Goethites in ochreous bands of Tertiary sands in NW Spain were found to contain structural Al with $\text{Al}/(\text{Fe}+\text{Al})$ of up to 0.2 (Barral Silva & Guitian Rivera, 1987). The bands shown in Plate 15.II are stained by hematite. In 20,000 year old, late Pleistocene sands in Denmark, amphiboles and pyroxenes have been identified as the main source of Fe for the formation of goethite and lepidocrocite (Postma & Brockenhuus-Schack, 1987). Studies of solution composition showed that under anoxic conditions, the ground water was undersaturated with respect to the two primary Fe silicates, which, accordingly, showed strong dissolution features (etch pits). The newly-formed oxides were deposited as globular coatings on mineral grains (Fig. 15.7). Another form of Fe oxide concentration in quarternary sediments appears as the so-called rattlestones: rounded, hollow concretions with a loose central part that rattles on being shaken. The concretions are cemented by high concentrations of laminated goethite, most probably formed by a reductive dissolution $\rightarrow$ migration of $\text{Fe}^{2+} \rightarrow$ reoxidation sequence of processes (van Loef, 2000), i.e. the normal process for concretion formation.

15.3.4

Ferricretes and bauxites

Concentrations of iron oxide are widespread in the weathering zones of rocks. Such concentrations may be “relative” i.e. due to removal of other rock elements or “absolute” i.e. due to the influx of dissolved Fe. The first type is formed *in situ* and is caused by the high stability (low solubility) of the Fe oxides precipitated during weathering. The second type, in which the Fe is usually more concentrated, forms preferably in low-lying regions of the landscape. Typical examples are the widespread Fe oxide crusts (so-called *ferricretes*) capping the deep weathering profile in the tro-

pics and subtropics (see also chap. 16). They were generally formed in the geological past, mainly from Tertiary to Pleistocene times and can therefore also be considered as soils (palaeosols). With further development of the landscape through incision of the rivers, areas protected by ferricretes were exposed and appear in the landscape as elevated, flat plateaux (mesa). This geomorphological process is referred to as relief inversion. Ferricrete mineralogy has been widely studied; the commonest Fe oxide minerals are hematite and goethite with some maghemite (Amouric et al., 1986; Anand & Gilkes, 1987, 1987a; Schwarz & Germann, 1993; Beauvais and Colin, 1993; Zeese et al., 1994, Beauvais and Roquin 1996) (for further references see Chap. 16). They show a wide range of crystal sizes and extent of Al substitution reflecting the environmental conditions during formation. An analogous, younger formation in the temperate region includes the so-called bog iron ores which are widespread in the former glacial valleys. Reflecting the cooler climate and their shorter age, bog iron ores are free from hematite and dominated by goethite and ferrihydrite (Schwertmann, 1959b; Schwertmann et al., 1982). Due to their occurrence as thin crusts over wide areas and their high P contents (Schlichting, 1965), ferricretes have been of no economic importance as Fe ores, except in prehistoric times (Iron age) and temporarily in war time. Bog iron ores have also been used in the past as building material, e.g. in NW Germany.

Tropical weathering materials are, however, used as Al ores if the Al (mainly as gibbsite, $\text{Al}(\text{OH})_3$) has been concentrated substantially (Valeton, 1972; Bardossy, 1983). These so-called *bauxites* (named after the French town of Les Baux) usually also contain Fe oxides in which part of the total Al is incorporated and is therefore not extractable by the alkaline extraction method (Bayer process) commonly used. Goethites and hematites in 69 Western Australian low-grade bauxites were highly Al-substituted (goethites 16–33 mol%; hematites 3–11 mol%), as would be expected from the presence of gibbsite in the ore (Anand et al. 1991).

15.4

Recent geological environments

There are various environments in which recent formation of Fe^{III} oxides on earth can be observed. Among these are active volcanoes, soils (see Chap. 16), rivers and lakes, oceans, both hydrothermal and cold springs, and biota (see Chap. 17). All these environments supply helpful information about the pathways of Fe^{III} oxide formation in the geological past of which they may be considered as present-day analogues. Since spectroscopic information about the red Martian surface became available, there has been much speculation about the possibility of past Fe oxide formation by surface weathering on Mars.

15.4.1

Terrestrial surfaces

Present-day formation of the potential, detrital parent material of red beds and iron stones may be seen in surface weathering. For example, hematitic material currently forms in warmer climates by rock weathering. One documented case involves dune sands which redden with age due to hematite formation (Norris, 1969). Radiometric and archaeometric dating of red dunes from various tropical regions have yielded ages <20000 years for the reddening process (rubefication) in sands free from detrital hematites (Gardner & Pye, 1981). Red dunes may, however, also receive their hematite pigment from transported sand or dust (detrital hematite) (see review by Blodgett et al., 1993). Walker (1967, 1967a) has described the current formation of hematite by weathering of ferromagnesian mineral grains in sands of Baja California which he considered the parent material for red bed formation.

15.4.2

Spring and ground water

Formation of ferrihydrite, a common initial phase in the genesis of Fe oxides, is a typical phenomenon wherever Fe^{2+} containing spring and ground waters appear at or near the aerated surface. Examples of this have been found in cold springs in the volcanic regions in Iceland (Plate 15.IV) and New Zealand (Childs et al., 1986; Henmi et al., 1980, Childs et al. 1982). Under such conditions Fe^{2+} is abiotically oxidized at a very high rate, thereby preventing the formation of better crystalline oxides. Soluble silicate, often present in these waters, will be coprecipitated with, or adsorbed at the surface of the ferrihydrite and may inhibit the transformation. Natural and artificial drainage lines transecting low-lying areas with high levels of ferrihydrite ground water may produce masses of ochreous Fe oxides dominated by ferrihydrite (Schwertmann & Fischer, 1973; Süsser & Schwertmann, 1983; Schwertmann & Kämpf, 1983; Murad, 1988; Fitzpatrick et al., 1992). Mössbauer spectra of such ferrihydrites are shown in Fig. 7.6. Clogging of tile drains by ferrihydrite (Plate 15. V) causes the malfunction of the artificial drainage system (Petersen, 1966; Kuntze, 1982). The absence of ferrihydrite in older sedimentary iron ores (see above) compared to the recent formations, indicates that ferrihydrite will transform to more stable, better crystalline forms with time and upon burial.

A quite different chemical environment exists in juvenile spring waters associated with volcanic activity (fumarols, boiling pools, streams), for example on the White Island, New Zealand. Yellow and brown surface deposits on andesite boulders were found to consist of jarosite, akaganéite and some goethite formed from a very acid, ferrihydrite water high in chloride and sulphate (Johnston, 1977). Granular ferrihydrite with some hairy goethite encrusting bacterial cells are the Fe oxides in actively forming, ochreous, zebra-textured precipitates in a 25 °C spring in an active volcano south of Kyushu Island, Japan (Plate 15.VI). The morphological similarity with well known ancient Banded Iron Formations (BIF) (see p. 416) suggests a similar formation process for the BIFs (Tazaki, 2000).

15.4.3

Deep sea

Another type of present-day formation of Fe^{III} oxides occurs on the ocean floor. Fe oxides are associated with Mn oxides and occur as crusts and nodules. The growth rate of these nodules is extremely low and has been estimated as being $2\text{--}15 \cdot 10^{-6}$ mm/yr (Rana et al., 1983). Two values lying in this range, viz. $6.6\text{--}7.8 \cdot 10^{-6}$ mm/yr for the last 150 000 years were derived from the decrease of Th and U isotope ratios ($234/238$ & $230/232$, respectively) in two Fe-Mn crusts in the Marshall Islands area (Chabaux et al. 1995, 1997).

These formations have attracted a lot of interest from scientists because they contain metals such as Co and Ni associated with the Mn oxides. A large range of trace elements was analysed in 21 crust samples from the Pacific (Koschinsky & Halbach, 1995). The nature of the Fe oxide minerals, however, has rarely been studied. A close association of clusters of vernadite ($\delta\text{-MnO}_2$) with those of ferrihydrite/feroxyhyte has been postulated by Ostwald (1984). Chukhrov et al. (1976a) identified feroxyhyte ($\delta'\text{-FeOOH}$) in deep-sea nodules from the Pacific Ocean, the Baltic, White and Kara Seas. In crusts from the Central Pacific that contained $150\text{--}200 \text{ g kg}^{-1}$ Fe, 4-line ferrihydrite with an extremely low magnetic hyperfine field of $45\text{--}46 \text{ T}$ at 4 K has been identified as the principal component. The increase in the magnetic hyperfine field to ca. 48 T after selective removal of vernadite with hydroxylamine suggested that the ferrihydrite was intergrown with the former mineral (Murad & Schwertmann, 1988). Iron-manganese nodules from ocean basins had significantly higher $^{54}\text{Fe}/^{56}\text{Fe}$ ratios than did the iron in igneous source rocks which is interpreted as being due to their biogenic genesis. The similarity with those in BIFs suggests a biogenic origin also for these nodules (Beard and Johnson, 1999).

15.4.4

Continental shelves

Iron-rich ($70\text{--}250 \text{ g kg}^{-1}$ Fe) sediments in the outer continental shelf of Northern New South Wales contained as the primary mineral, authigenic berthierine, $(\text{Fe,Al})_3(\text{Si,Al})_2\text{O}_5(\text{OH})_4$, which subsequently transformed to goethite (Marshall, 1983). Increasing amounts of ferrihydrite in pelagic clay sediments in the Southwestern Pacific Basin NE of New Zealand were correlated with a decreasing rate of total sedimentation, i.e. a decreasing rate of burial (Johnston & Glasby, 1982). In anoxic, marine sediments from the Long Island Sound and the Mississippi Delta, Canfield and Berner (1987) found magnetite of both detrital and biogenic origin, which transformed to pyrite at a rate which depended on the S^{2-} concentration and the surface area of the magnetite.

15.4.5

Lakes and streams

Recent Fe oxide formation also takes place in fresh water lakes especially those near the shore. These so-called lake iron ores are widespread in glacial Pleistocene areas, such as Scandinavia. It is considered that the iron is mobilized in podzolized soils in the surrounding morainic landscape as iron-organic complexes and transported into the lakes. In the anoxic environment of the carbon-containing bottom sediments, the iron is reduced and diffuses upwards along an Eh gradient into the oxygenated water column where it precipitates as Fe^{III} oxides (Halbach, 1976). The oxides occur as nodules and crusts containing up to 400–450 g kg⁻¹ Fe. The growth rate of these nodules was estimated using the ¹⁴C method as $3\text{--}4 \cdot 10^{-3} \text{ mm yr}^{-1}$ (Halbach, 1976). They consisted of goethite and ferrihydrite in variable proportions, which probably depended on the rate of Fe oxide accretion (Schwertmann et al., 1987). The cool climate of these areas and the high water activity prevents hematite formation. The goethites exhibited low Al substitution when formed in a sandy bottom sediment and medium substitution in clayey sediments, presumably because more Al is available in the latter (see Chap. 16). This type of Fe oxide formation still occurs in lakes.

In eight Canadian oligotrophic lakes, the Fe oxides which were collected at the water/sediment interface over 3 to 12 months consisted mainly of lath-shaped and filamentous lepidocrocite with some globular ferrihydrite (Fortin et al. 1993). They form by oxidation of Fe²⁺ migrating upwards from the reduced part of the sediment to the aerated upper part and the surface. Microbial cells and debris appear to act as templates causing fairly high carbon/Fe mole ratios of 2.2–5.4. The conditional adsorption constants calculated from the concentration of various metals (Ca, Cd, Cu, Mg, Ni, Pb, Zn) on the iron oxide surface and in the aqueous phase were close to laboratory values obtained with well defined oxides (Tessier et al. 1996). Similar globular, Fe-rich particles with a maximum concentration at just below the depth where no O₂ was detected, were identified in two Swiss lakes. EDS spectra showed C, P and Si to be the main constituents besides Fe (Perret et al. 2000) suggesting ferrihydrite to be the major mineral present.

Tipping et al. (1981) described suspended Fe-rich precipitates in a eutrophic lake in Cumbria, U.K. Ellipsoidal particles ca. 0.1 µm wide and 0.2–0.5 µm long resembling bacterial cells and with 300–400 g kg⁻¹ Fe and 40–70 g kg⁻¹ humic carbon have been found in concentrations of 10¹¹–10¹² particles per liter corresponding to 3 mg Fe L⁻¹. These particles were negatively charged over the pH range of 4–10, probably because of adsorbed humics, silicate and/or phosphate (see Chap. 11). Fe-rich particles, remarkably homogenous in their shape (globular) and size (~100nm) were isolated from a eutrophic lake in Switzerland. Besides Fe, they contained some Si, P and Ca and had a high colloidal stability, so that they would settle only if attached to coarser biogenic debris (Pizarro et al. 1995). In peaty bogs, stagnant pools are often covered with iridescent films which are frequently mistaken for oil spills. In fact these are usually very thin films of mixed-valent Fe oxides. In all these cases, the specific Fe oxides have not been identified, but ferrihydrite is the most likely can-

didate. The flocculation mechanism of Fe-rich particles in an estuarine environment has been studied by Mayer (1982).

Where stream waters contain Fe, boulders on the bottom are often coated with Fe oxides with no relationship to the petrography of the boulders. The amount of Fe oxide deposited is around a few mg cm^{-2} (Schwertmann and Friedl, 1998) and the annual accretion rate is in the range of $100 \mu\text{g cm}^{-2}$ (Carpenter & Hayes, 1980). Suspended particles in brownish, drainage waters from tropical soils in the Cameroons, in which goethite with some hematite were identified, are transported from the soil profile to a spring and then to the water course (Olovie-Lauquet et al. 2000).

Another type of recent Fe^{III} oxide formation occurs in streams and lakes fed by pyrite oxidizing waters, either natural or from rain (Plate 15.VII) seeping through pyritic rocks or mine spoils and abandoned shafts (acid mine drainage; AMD). These waters are rich in H_2SO_4 and Fe^{2+} . In an aerobic environment the Fe^{2+} will be oxidized by autotrophic bacteria (esp. *Thiobacillus ferrooxidans*) even at very low pH (2–3) and a range of Fe^{III} minerals will form depending on the pH and SO_4^{2-} concentration (see for example Nordstrom, 1982; Chapman et al., 1983; Lazaroff et al., 1982, 1985; Karathanasis et al., 1988, 1995; review by Bigham & Nordstrom, 2001). Among these minerals are various Fe^{III} sulphates, different jarosites, schwertmannite, goethite and ferrihydrite (Bigham et al., 1990, 1992, 1994; Milnes et al., 1992; Fitzpatrick et al., 1992; Herbert, 1995; Yu et al. 1999; Singh et al. 1999; Carlson et al. 2002). The sedimentation rate of schwertmannite at pH ~3 in a 40 cm water column from an artificial lake formed by lignite mining was between 0.6 and $4.2 \text{ g Fe m}^{-2} \cdot \text{d}^{-1}$ (Peine et al. 2000).

The above genetic association of minerals has also been found in the Alps in a natural creek, draining a pyritic schist exposed at the surface. As more and more non-acid, fresh water enters the creek, the formation of jarosite and schwertmannite is replaced by that of goethite and ferrihydrite (Schwertmann et al., 1995; Bigham et al., 1995) (see also Plate 13.I). An occurrence of natural schwertmannite was reported in a lake in Honshu Province, Japan, into which anoxic groundwater derived from pyritic volcanoes, enters the lake floor (Childs et al. 1998). As expected from its metastability with respect to goethite, and as shown in the laboratory experiments (Bigham et al. 1995) and observed in natural (Childs et al. 1998) and acid mine drainage (AMD) lakes (Peine et al 2000), schwertmannite transforms to goethite. The rate may, however, be slow unless the pH of the AMD waters rises due to reaction with rock minerals. The same happens with jarosite whose transformation may have environmental relevance if it contains Pb as is the case for plumbojarosite $\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12} \cdot \text{H}_2\text{O}$. The lead may be released as the precursor hydrolyses to an Fe oxide which in turn, may adsorb the lead on its surface (Hochella et al. 1999). Effective scavenging of the rare earth elements and yttrium by ferrihydrite was found in Fe-rich precipitations from the Nishiki-numa acid-sulphate spring in Japan (Bau et al. 1998).

15.4.6

Hydrothermal marine environments

Hydrothermal marine Fe oxide formation from vents, a process thought to be responsible for the genesis of the Lahn-Dill type of Fe ore, can be observed nowadays in various parts of the world (Bäcker, 1973; Hannington & Jonasson, 1992). A large range of minerals is formed under these conditions, but Fe^{III} oxides often predominate. Well studied examples include the precipitates from hot brines in the various deeps of the Red Sea, e.g. the Atlantis and Thetis Deeps, the submarine volcanoes of Vanuatu in the South-West Pacific, and the warm springs around the island of Santorini, Greece.

Goethite, lepidocrocite, akaganéite, hematite and wüstite as well as Fe silicates have been identified in the well-known hydrothermal deposits from the Atlantis and Thetis Deeps of the Red Sea volcanic area at a depth of ca 2000 m (Holm et al., 1983; Singer & Stoffers, 1987; Taitel-Goldman et al. 1997; 2001; 2002), but just as frequently, the oxides were described as amorphous or poorly ordered due to their presumably rapid formation upon entrance of Fe^{III} containing solutions into the weakly alkaline, hot marine environment (Harder, 1960; Puchelt, 1973; Danielson et al., 1980; Exon & Cronan, 1983). In the Atlantis II Deep precipitate, a very well-ordered hematite with idiomorphic crystals and a magnetic hyperfine field at RT as high as 51.3 T was associated with an extremely poorly-ordered hematite, higher in the column; the latter showed strongly and anisotropically broadened XRD lines (104 much broader than 110) and a hyperfine field as low as 47.2 T. The TEM in Fig. 15.8 shows the pseudo-hexagonal shape of well-crystalline, tiny granular particles a few nm in size as well as defective rings 50–100nm across and 2.4 to 2.8nm thick (Schwertmann et al., 1998) also looked upon as dishes (Taitel-Goldman et al. 2001). All three were interpreted as being different morphologies of hematites, the poorly crystalline form probably being siliceous hematite (based on EDX) (Schwertmann et al. 1998). Siliceous ferrihydrite, hisingerite and poorly crystalline nontronite were also suggested as compounds (Taitel-Goldman et al. 2001). An XRD line shift towards groutite, the MnOOH analogue of goethite, established that the goethite is Mn-substituted (Anschütz and Blanc, 1995). In the Thetis Deep, akaganéite (Fig. 15.8), lepidocrocite and magnetite have been described (Scholten et al., 1991; Taitel-Goldman et al. 2002). The layer-wise occurrence of different Fe oxides (and other minerals, such as siderite, manganite and various clay silicates), suggests variable conditions of formation in the sediment column with respect to the chemical composition of the brine, temperature, redox potential, rate of formation, etc. Fe-rich smectites probably formed by the reaction of poorly-ordered Fe^{III} oxide with dissolved silicate (Cole, 1983; Singer & Stoffers, 1987).

A 2-line ferrihydrite deposit is also formed from hydrothermal fluids at 60–93 °C upon mixing with sea water near the coast of Amberlite Island, Papua New Guinea. The hydrothermal waters are rich in As which is almost completely captured by the ferrihydrite (50–60 g As/kg), thereby hindering the formation of better crystalline Fe oxides and also preventing any toxic effects on the marine biota (Pichler, et al. 1999; Pichler and Veizer, 1999; Rancourt et al. 2001). Spherical, 10nm-sized, Si-containing,

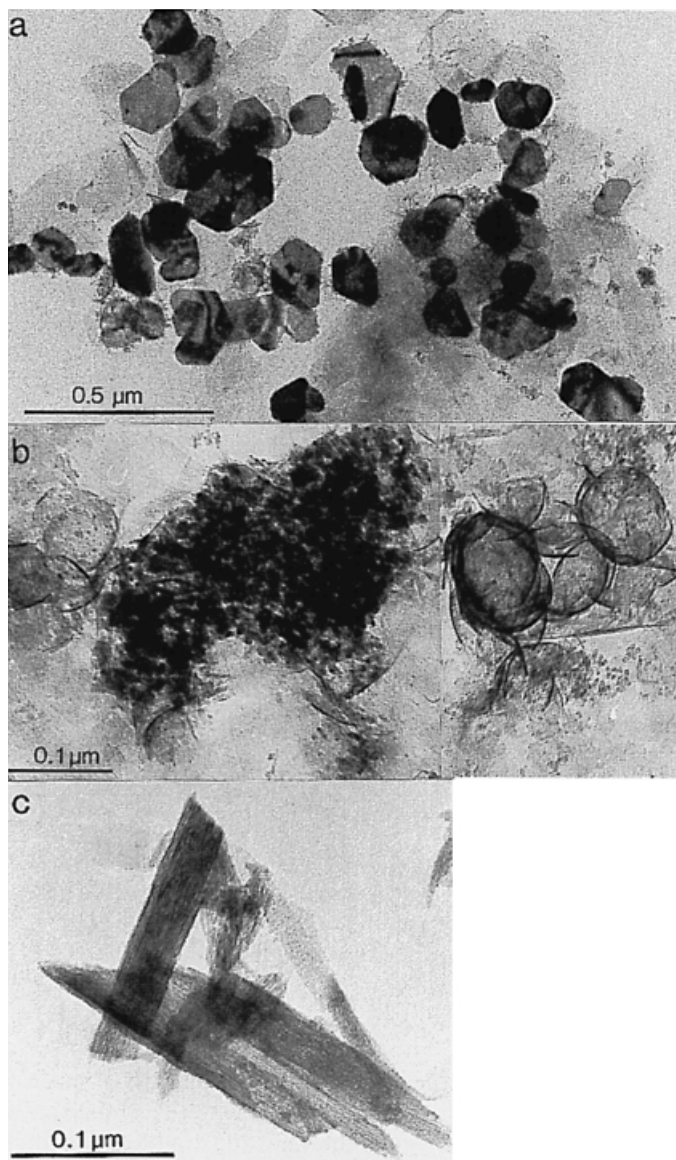


Fig. 15.8 Well crystalline euhedral platy hematite (a), poorly crystalline spherical Si-containing hematite together with ring-like layer Fe-silicates (?) (b), and akaganéite (c) from the Atlantis Deep, Red Sea, (Photo H.-Ch. Bartscherer) (Schwertmann et al., unpubl.)

2-line ferrihydrite particles arranged in 2–300nm long chains were detected at the site of a hydrothermal vent (5–50 °C) on the Southern Explorer Ridge in the NW Pacific at a depth of ca.1800m. Here, bacterial surfaces were suggested as the substrate for mineral nucleation (Fortin et al. 1998).

15.4.7

Martian surface

Geochemical, magnetic and spectroscopic information obtained by the various spacecraft missions revealed that bright regions of the surface of the red planet (Plate 15.VIII) may be covered by iron-rich phases, especially Fe-rich silicates and Fe oxides including magnetic ones. A set of permanent magnets fixed to the Pathfinder Lander has attracted considerable amounts of magnetic particles (Madsen et al., 1999). These observations provide evidence for chemical weathering at Mars' surface, in an earlier atmosphere, by which Fe^{II} from primary minerals was oxidized to form Fe^{III} containing, secondary minerals (Burns, 1993). The possible deficiency in oxygen as an oxidant could have been overcome by photostimulated oxidation with UV-radiation (Lundgreen et al. 1989). Elongated, single-domain magnetite crystals in the Martian meteorite ALH84001 found in Antarctica are similar in shape to biogenic magnetite and have been considered by some to be Martian magnetofossils (Mckay et al., 1996); they initiated further discussion about the existence of life on early Mars under microaerobic conditions similar to the environment of magnetotactic bacteria on earth (Thomas-Keprta et al., 2000; Thomas-Keprta et al., 2001) – although it has been questioned whether the morphology proves a biogenic origin (Buseck et al., 2001).

Since no material from the Martian surface is yet available, a range of presumed synthetic and terrestrial analogues with respect to the spectral, chemical and magnetic properties (known to date) of the bright regions of the Martian surface (e.g. the Tharsis and Amazonis planes) has been studied (for a summary see the special issue of *Geochim. Cosmochim. Acta* 57, 1993 and Morris et al. 2000). The main emphasis was on the red pigment material at the Martian surface; this shows strong absorption in the visible range between ≈ 400 and 750 nm, typical of most fine-grained Fe oxides and a shallow band in the near infrared (≈ 860 –930 nm) (see Chap. 7) as well as having a saturation magnetization of ca. $42 \text{ A m}^2 \text{ kg}^{-1}$ and a definite sulphur content. These data were obtained from the Viking (1976) and the Pathfinder (1997) missions and are summarized by Bell et al. (2000) for soils and by McSween et al. (1999) for rocks on Mars.

As a *synthetic* analogue of Martian soil, Morris and coworkers (Morris et al., 1989; Morris and Lauer Jr., 1990; Morris et al., 1992) suggested nanophase Fe oxide with a particle size $< 10 \text{ nm}$, two broad XRD lines similar to 2-line ferrihydrite, 70 g kg^{-1} water, a magnetic ordering temperature $< 13 \text{ K}$ and a B_{hf} of 50.4 T at 4 K, somewhat higher than that of 2-line ferrihydrite. Such a compound was synthesized either by producing the Fe oxide in the presence of an SiO_2 gel, or by thermal decomposition of trinuclear aceto-hydroxy-iron^{III}-nitrate at 210 °C. Other compounds suggested as resembling Martian soil were “amorphous Fe^{III} oxide gels” (ferrihydrite?) (Evans

and Adams, 1980), altered volcanic glass (palagonitic material (Allen et al., 1981)) and Fe-smectites (Banin et al., 1985) as well as ferrihydrite-smectite aggregates (Bishop et al., 1993). Based on the sulphur content, an Fe hydroxysulphate (Berner, 1993) and schwertmannite (Burns, 1994); Bishop and Murad, 1996) were further candidates. It was proposed that schwertmannite forms by aerial oxidation of Fe^{2+} in acidic, sulphate, saline melt waters (Burns, 1994) and that it may form interlayers in smectite (Bishop et al., 1995). Analysis of ISM spectra of Mars (0.76–3.2 μm) suggests a higher abundance of alteration products including iron oxide hydroxides, sheet silicates and hydrated sulphates such as schwertmannite in the Tharsis-Arabia region of Mars (Murchie et al., 2000). To cope with the elevated magnetic susceptibility, maghemite formed from lepidocrocite by impact events has also been suggested (Torrent and Barron, 2001).

Examples of possible *natural* analogues are weathering rinds and dust from Hawaii, Iceland and other volcanic islands.. They typically contain iron oxides/oxide hydroxides and a consortium of poorly crystalline silicates including allophane and hisingerite (Morris, et al. 1993; 1998; 2000; Bishop et al. 1998, 2002). A nanophase Fe^{III} oxide with an SED pattern consistent with that of hematite (intense rings at 0.25 and 0.15 nm, and weak rings at 0.27, 0.22, 0.17, 0.144 and 0.082 nm) was identified in the amorphous Si-Al-matrix of a palagonitic tephra from a Hawaiian volcano. Some support has also been gained from a simulation of the Magnet Array Experiment on-board the Pathfinder Lander performed at the Mauna Kea volcano (Hawaii), (Morris et al. 1999).

It is obvious from these experiments that the absorption spectrum of the Martian red surface can be simulated reasonably well by a non-unique variety of Fe rich phases or their mixtures as can the weak magnetism, so that a positive identification will probably only be possible, following further in situ analyses and/or sample return and analysis in the lab. Two Mars Exploration Rovers (MERs) are due to arrive at Mars in 2004 and will attempt to analyze rocks and soils on the surface using several small spectrometers, including PanCAM (an extended visible region spectrometer), MiniTES (a thermal emission spectrometer), APXS (alpha proton X-ray spectrometer measuring the major elements), Mössbauer (run at current local temperature), as well as a 5-level magnet array similar to that on-board the Pathfinder Lander.

15.5

Iron fractionation in sediments

As for soils, similar chemical extraction methods have been developed to determine the speciation of Fe in sediments (Heron et al. 1994; Kostka and Luther III, 1994). For Fe oxides, some modifications of the scheme used in soils are needed. In particular, oxalate may not be applied if large amounts of Fe^{II} are present because in oxalate solution, Fe^{2+} will catalyze the dissolution of better crystalline Fe oxides such as goethite and, therefore, the method will not be specific for ferrihydrite. Fe bound in sulphides and carbonate is extracted by HCl prior to dithionite which, as in soils, extracts most of the Fe^{III} oxides. The latter can also be extracted by a Ti^{III} -EDTA solu-

tion. In a 4-step extraction method (acetic acid, hydroxylamine, oxalic acid, residual) applied to 21 Fe-Mn-crust samples from the Pacific, 30–50% of the total Fe dissolved in step 2 and 50–70% in step 3, but this could not be correlated with definite Fe minerals (Koschinsky & Halbach, 1995).

Appendix

Isotope ratios of goethites have been used to gain information about the environmental conditions under which they and, thus, the rocks (or soils; chap. 16) in which they occur, have been formed. Based on the known dependence of the hydrogen (D/H) and oxygen ($\delta^{18}\text{O}$) fractionation factors, Yapp (2000) deduced that the formation temperatures of 32 different goethites ($\delta^{18}\text{O}$: –224 to –93‰; δD : –15.5 to +2.8‰) were between 0 and 30 °C for average meteoric water. These values are either concordant with the present average surface temperature or somewhat higher. Another group of goethites may have formed when the global climate was warmer than present (20–35 °C) and a third group was formed at a temperature between 19 and 69 °C, i. e. in environments of subsurface heat sources. A ~3‰ increase in the oxygen isotope ratio in a holocene ferricrete chronosequence of the NE Yellowstone region was interpreted as indicating a decrease in monsoonal intensity over the last 9000 yr B.C. (Poage et al. 2000).

16

Soils

16.1

Soils – a unique environment for iron oxide formation in terrestrial ecosystems

A soil mantle, the so-called *pedosphere*, covers most of the surfaces of the continents. It is the product of a long-lasting interaction between the atmosphere, biosphere and hydrosphere on the one hand and the lithosphere on the other. Rocks are usually formed under conditions different from those at the earth's surface, and, once exposed at the surface, are unstable and deteriorate – they weather. The weathering processes which occur spontaneously are accompanied by a decrease in enthalpy and a range of new stable minerals forms. Parameters guiding these transformations are the constituents of the atmosphere (atmospheric pressure and precipitation, oxygen, temperature, frost and dissolved constituents in the rain water) and the biosphere (organic and inorganic compounds, plant roots, soil fauna and flora).

Almost all rocks contain at least some iron. The more important minerals, in which Fe is a major constituent, are given with their Fe contents in Table 16.1. In all of these minerals except magnetite, iron is exclusively or predominantly in the bivalent state. During weathering, the iron is released from these minerals and “secondary”, pedogenic iron minerals are formed. The most important ones are Fe-containing clay silicates and Fe oxides but under reducing conditions, Fe carbonates, sulphides and phosphates may also be formed.

Tab. 16.1 Major iron-containing minerals in primary rocks

Name	Formula	Fe content/mg g ⁻¹	
		FeO	Fe ₂ O ₃
Biotite	K(Fe ^{II} ,Mg) ₃ Si ₃ AlO ₁₀ (OH) ₂	30–280	1–210
Pyroxene (augite)	(Ca,Mg,Fe ^{II} ,Al,Ti) ₂ (Si,Al) ₂ O ₆	40–210	4–76
Amphibole (hornblende)	Ca ₂ (Mg,Fe,Al) ₅ (Si,Al) ₈ O ₂₂ (OH) ₂	< 90	2–230
Olivine	(Mg,Fe ^{II}) ₂ SiO ₄	80–120	–
Ilmenite	FeTiO ₃	473*	–
Magnetite, titanomagnetite	Fe ₃ O ₄ , Fe _{3-x} Ti _x O ₄	310*	690*
Pyrite	FeS ₂	817*	–

* theoretical content

Soil iron oxides vary greatly with respect to mineral species, concentration and crystal properties; they depend on the environmental conditions in the pedosphere which vary in space and time. This variation originates in part because soil is a heterogeneous arrangement of solid matter and pores (ca. $0.35\text{--}0.65\text{ m}^3\text{ m}^{-3}$) filled with a gaseous (soil air) and an aqueous phase (soil solution). The soil *temperature* depends mainly on the geographical position and ranges from permanent frost in the tundra and arctic regions to as high as ca. 60°C near the soil surface in the arid tropics. It decreases with soil depth and fluctuates with the season. Dry soils are warmer than wet soils as the heat capacity of water is much higher than that of air. Although the composition of the *soil air* is often similar to that of the atmospheric air, it may deviate from this considerably. Because O_2 is consumed and CO_2 is produced in soils by biota and because diffusion of these gases may be hindered, the pressure of O_2 may drop to zero (atmosphere 21 kPa) and that of CO_2 may go up to ca. 2 kPa (atmosphere 30 Pa).

The *soil solution* is held against gravity in the soil because it is bound to the particle surfaces and also held in the pores by menisci. The water vapour pressure (water activity) is therefore lowered against that of free water (activity = 1), a factor which may affect the formation of Fe oxides. The aqueous phase in soils is a dilute electrolyte solution containing a range of dissolved compounds. The soil pH ranges from slightly alkaline to strongly acid, and the redox potential, Eh, from strongly reducing to oxidizing. Compounds such as silicate, phosphate and organics as well as toxins in the soil solution may interfere with crystal growth because they interact with the crystal surfaces (see Chap. 11). Often, Fe oxides are precipitated at the surfaces of other minerals.

The physical and chemical parameters which influence iron oxide formation vary with *time* and *space*, e.g. through changing water/air content. Microenvironments exist in pores of different sizes and with different degrees of filling. For example, hematite was identified in coatings at the (dry) surface of a basalt boulder, whereas goethite occurred in a nearby (moister) crack (Bender-Koch et al., 1995a). In another case, goethite was the dominant oxide next to the root surface, whereas lepidocrocite predominated a few mm away from it (Schwertmann & Fitzpatrick, 1977). Often, however, the exact conditions under which Fe oxides form are difficult to determine.

Pedogenic iron oxides store information which allows the *age* of a soil in different parts of a profile to be determined. This information can either be derived from the weak remanent magnetization which leads to orientation of the oxide crystals within the geomagnetic field during their formation, or from isotope differentiation which reflects the climate during pedogenesis. Using the paleomagnetic signal of hematite, the rate of soil formation (weathering) in a 54 m-deep tropical soil in French Guiana was determined to 11.3 m/Ma (Theveniaut and Freyssinet, 1999). In a 30 m deep soil profile from the same area, the $\delta^{18}\text{O}$ values of goethite (and kaolinite) could be used to distinguish the upper 20 m which formed under a paleoclimate from the lower 10 m whose $\delta^{18}\text{O}$ levels were those of the present atmosphere (Girard et al. 2000).

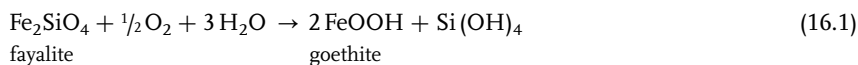
In conclusion, the pedosphere is an environment of active mineral formation and transformation and exhibits a large variation in formation parameters in space and time over a range of scales. It openly and permanently communicates with neigh-

bouring compartments of the ecosystem (atmosphere, biosphere, hydrosphere, lithosphere) so that equilibrium is usually not reached. Therefore, the possibility of predicting the various forms of Fe oxides (and other minerals) from thermodynamic information is limited. Chapters on iron oxides in soils are published by Schwertmann & Taylor (1989) and, recently, by Bigham, Fitzpatrick & Schulze (2002).

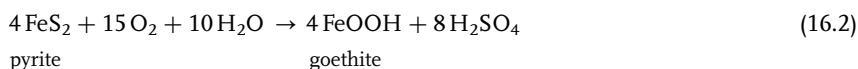
16.2

Iron oxide formation in soils

Primarily, Fe is released from the lithosphere into surface environments including soils by weathering of primary silicate and sulphide minerals (Tab. 16.1). In the presence of O₂ and H₂O and in the common pH range (>2) of surface environments, the released Fe^{II} is oxidized to Fe^{III} which in turn, is immediately hydrolysed to form Fe^{III} oxides and oxide hydroxides. For Fe^{II} silicates these reactions involve breakage of an Fe^{II}-O-Si bond and the formation of Fe^{III}OH and SiOH groups. For example, goethite may be formed from the oxidation and hydrolysis of olivine (fayalite) through the reaction:



Similarly, the breakdown of iron sulphide, (pyrite), may be written as:



In these reactions oxygen serves as the electron acceptor. Micro-organisms may or may not be involved in the Fe^{II} to Fe^{III} oxidation. The higher the pH of the solution, the more rapidly will the dissolved Fe²⁺ ions be oxidized and the more likely is it that abiotic oxidation will prevail. On the other hand, under very acid conditions (pH < 3), oxidation and the formation of Fe^{III} minerals must be mediated by micro-organisms (see Chap. 17).

The stability of the various lithogenic Fe^{II} minerals to oxidative-hydrolytic weathering varies greatly and depends mainly on the crystal structure and also on particle size. Fe^{II} silicates are generally more stable than sulphides (pyrite, marcasite) and carbonates (siderite, ankerite). Of the large group of rock silicates, those containing Fe^{II} are the least stable members. This is because in an aqueous, aerobic environment often existing in soils, Fe^{II} will be readily oxidized and this weakens the structure. Of the Fe^{II} silicates, nesosilicates (olivine) are less resistant than chain silicates (pyroxenes) and phyllosilicates (biotite). Colour measurements by visible microspectroscopy suggested that the brownish, 0.5mm thick rind of a biotite grain in weathered granite consisted of goethite and ferrihydrite (Plate 16.IV) (Nagano et al. 2002). The primary Fe oxides, magnetite, titanomagnetite and ilmenite are usually fairly stable.

Mechanisms of Fe oxide formation from the above Fe minerals have been derived from the type of spatial association between the minerals. Examples are olivine (Eggleton, 1986); biotite (Wilson, 1970; Wilson & Farmer, 1970; Farmer et al. 1971; Gilkes & Suddhiprakarn, 1979); hornblende (Walker et al., 1967); chlorite (Smith, 1959; Bain, 1977); pyroboles (Berner & Schott, 1982); hornblende, chlorite, ilmenite (Anand & Gilkes, 1984, 1984a); garnet (Velbel 1984; 1993); magnetite (Gilkes & Suddhiprakarn, 1979a, Anand & Gilkes, 1984b); ilmenite (Suresh Babu et al. 1994). Possible pathways from the parent mineral to the Fe oxides are: (1) Topochemical (solid-state) transformation as for magnetite $\rightarrow$ maghemite; (2) Removal of Si with Fe remaining in much the same structural arrangement after oxidation as shown for the olivine $\rightarrow$ goethite transformation (Fig. 16.1); (3) Topotactic, oriented crystallization of the iron oxide at the surface of the parent mineral which acts as a template as shown for akaganéite growth on biotite (Farmer et al., 1971) or chlorite flakes with goethite [010]//silicate [010]; (4) Pseudomorphosis as shown for goethite from pyrite or siderite or for hematite from magnetite and ilmenite; (5) Non-oriented coatings on the parent mineral's surface; (6) No relationship when the released Fe^{2+} ion is oxidized not at the place of release, but only after some migration. It generally holds that it is the environmental conditions rather than the particular structure of the parent mineral which dictate the type of Fe oxide formed (see below). In addition, the environmental conditions rather than the thermodynamic stability may be decisive in this respect.

Once formed, their high thermodynamic stability usually ensures that Fe^{III} oxides persist for long periods of time. Their movement within the soil mantle or the land-

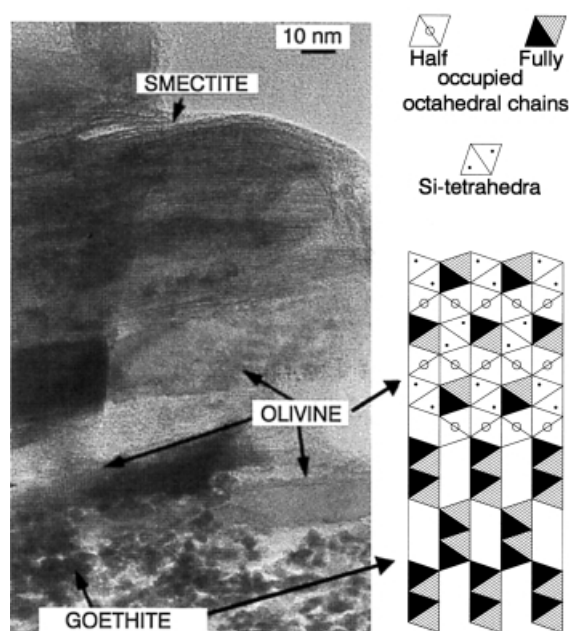


Fig. 16.1 Electronmicrograph of a thin section of an olivine weathered to goethite and smectite (Eggleton, 1986; with permission).

scape can take place mechanically together with other soil particles, for example by clay migration down the soil profile or lateral surface erosion. They can also be dissolved, either by complexation with organic compounds or by reduction. The latter takes place only in *anaerobic* environments via microbial metabolic activity:



This requires a biomass which can be metabolized. The process usually involves enzymatic transfer of electrons by micro-organisms from the decomposing biomass (represented in the above equation as CH_2O) to the Fe^{III} in Fe^{III} oxides. As seen from eq.16.3, reduction consumes protons and is, therefore, favoured, the lower the pH (see also Chap. 12). It usually takes place when all pores are filled with water (see reviews by Fischer, 1988 and Van Breemen, 1988). Biotic reduction of Fe oxides is now recognized as an important process in the oxidation (metabolism) of organic pollutants in soils by dissimilatory, iron-reducing bacteria.

The Fe^{2+} formed this way is mobile in the soil mantle and moves in (by diffusion) or together with (by convection) the soil water until it reaches aerobic environments where it is reoxidized and reprecipitated, often as Fe^{III} oxides. Such processes lead to characteristic colour patterns in the soil mantle (*redoximorphosis*) which reflect the mobilizing/immobilizing processes (Schwertmann & Fitzpatrick, 1992; Schwertmann, 1993). The distances over which Fe^{2+} migrates range from between 10^{-3} – 1 m within soil profiles to up to 10^4 m in landscapes.

16.3

Iron oxide content and soil development

The Fe oxide *content* of a soil may vary between <1 and several hundred g kg^{-1} . It depends on the type and Fe content of the parent rock and on the maturity of the soil. As soil develops, more and more of the original Fe-bearing minerals decompose and most of their Fe is precipitated as pedogenic Fe oxides (McFadden & Hendricks, 1985). In highly weathered soils, therefore, only the most stable, lithogenic Fe minerals such as ilmenite remain; the rest of the iron has been converted to pedogenic Fe oxides. Eventually, the Fe-containing clay minerals that formed initially will also decompose and release their Fe to form Fe oxides. In typical soils on calcareous loess and till from the Würmian era in Western Europe, the Fe oxide formation rate was estimated to be ca. 0.1 – $0.3 \text{ g Fe/m}^2 \cdot \text{yr}$ (Schwertmann, unpubl.).

The degree of transformation can be quantified analytically through the ratio of Fe in the oxides (commonly extracted with the strong reductant sodium dithionite (Fe_d)) to the total amount of Fe (Fe_t) and also by the ratio of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$, because the iron located in the primary minerals of the parent rock is predominantly Fe^{II} . With age, the ratio Fe_d/Fe_t gradually approaches unity and the total $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ approaches zero (Leigh, 1996). Therefore, both can serve as an indicator of the maturity of a soil as a function of time (*chronosequence*) (e.g. Italy: Arduino et al., 1984; Nepal: Bäumler et al. 1991, Spain: Simon et al. 2000; USA: Barret, 2001; Egli et al. 2001). The

younger soils of the formerly glaciated regions of the northern hemisphere (ca. $1-1.5 \cdot 10^4$ years old) have Fe_d/Fe_t ratios of ca. 0.2–0.3, whereas values of up to 0.9 are found in the well developed and highly matured, deep soils of the humid tropics (e.g. the soils on the former Gondwanaland continent) which have formed over much longer periods of time (10^7-10^8 years) (Fitzpatrick, 1988). In a sequence of pleistocene soils of different ages from the Blue Ridge Mts., USA, $\text{Fe}_t^{\text{II}}/\text{Fe}_t^{\text{III}}$ decreased from 3 to <1 (Leigh, 1996). Naturally, the soil environment also plays an important role in the rate at which the above ratios change with time.

To characterize the Fe oxide mineralogy of soils, differential dissolution techniques which are operationally defined, but backed by mineralogical analysis, are frequently used. The most common extractant of the total amount of Fe oxides is a strong reductant, viz. Na dithionite (Fe_d), combined with Na carbonate for pH buffering and Na citrate for keeping the extracted Fe in solution (Mehra & Jackson, 1960); hydroxylamine hydrochloride, a weaker reductant, appears to be too weak for this purpose (La Force & Fendorf, 2000). Usually, if all pedogenic Fe oxides are extracted, the sample should have lost its typical brownish-yellowish-reddish colour and appear bleached. A second widely applied extractant is acid NH_4 -oxalate (pH 3) (Fe_o) (Tamm, 1922, Schwertmann, 1959, 1964, 1984b; McKeague & Day, 1966), which extracts the poorly crystalline fraction of total Fe oxides, mainly ferrihydrite, but possibly also some Fe from allophanic and Fe-humic compounds (see Chap. 12). A widely used parameter is then the ratio of oxalate to dithionite-extractable Fe, (Fe_o/Fe_d) which ranges in soils from between almost 0 and 1. Mineralogical analysis (XRD, Mössbauer spectroscopy) has shown that Fe_o approximates the amount of ferrihydrite present and a decrease in Fe_o/Fe_d reflects the transformation of ferrihydrite to better crystalline oxides.

Various soil groups and soil horizons are represented by characteristic ranges of the ratio Fe_o/Fe_d (Blume & Schwertmann, 1969). In general, the highest ratio within a particular soil profile is usually found in the topsoil, reflecting the effect of organics in impeding the crystallization of Fe oxides. Below the surface horizon in the mineral soil (B horizon), Fe_o/Fe_d varies greatly. Humid temperate soils in glacial and periglacial regions show Fe_o/Fe_d ratios of between 0.2 and 0.4 reflecting association of poorly crystalline goethite with some ferrihydrite, whereas ratios of <0.1 prevail in older, more mature tropical soils (Ultisols, Oxisols) containing only the better crystalline goethite and hematite. Redoximorphic soils with a more active redox dynamics show Fe_o/Fe_d values of between 0.4–0.6, whereas even higher ratios of 0.8–1.0 are frequently met in podzol B horizons where Fe oxides (mainly ferrihydrite) form in a cool, humid climate under acid conditions in the presence of high amounts of organics. A decreasing Fe_o/Fe_d may also be used to characterize the increasing maturity of soils within a chronosequence (Simon et al. 2000).

The oxalate method also provides information about the capacity of soils to adsorb certain compounds such as phosphate, arsenate etc. and to supply Fe to the plant root because both are influenced by their ferrihydrite content. In fact, a negative correlation was found between Fe_o and the severity of chlorosis of sorghum in calcareous soils of Texas (Loeppert & Hallmark, 1985) and Fe_o has been used for the sandy soils of the Netherlands to predict their capacity to adsorb phosphate and prevent P

contamination of the nearby groundwater (Freese et al., 1992). Oxalate-extractable phosphate, silicate and trace metals may be regarded as being associated with ferrihydrite. The oxalate method was recently criticised because oxalate also dissolves magnetite and Fe-containing allophane-imogolite, and a citrate-ascorbate extractant (pH 6) has been suggested instead. There was, however, substantial scattering in the relationship between the Fe extracted from a large variety of (63) soils by the two methods with no statistical difference from the 1:1 relation except for allophane-imogolite soils (Andisols) (Reyes & Torrent, 1997). Another method of differential dissolution used for soils is the separation of maghemite from goethite and hematite by an extraction with 1.8 M H_2SO_4 at 75 °C for 2 hours (Schwertmann & Fechter, 1984; Da Costa et al., 1999).

16.4

Occurrence and formation

16.4.1

Historical aspects

Iron oxides in soils have in common that they are of extremely small crystal size and/or low crystal order. This, in combination with their low concentration (only tens g kg^{-1} in most soils) explains why soil iron oxides have escaped identification for a long time in spite of their obvious existence as seen from the soil colour. In the past, therefore, Fe oxides in surface environments have been considered to be amorphous to X-rays and often called “limonite”, which mineralogically, is an obsolete term. Furthermore, in order to identify the clay minerals in soils properly, Fe oxides are usually removed before X-ray diffraction methods are applied (Alexander et al., 1939; Mehra & Jackson, 1960).

For all these reasons, the various well-defined Fe oxide species have only been identified in soils at a relatively late stage. Although the German poet J. W. von Goethe, provided a detailed description of the red (hematitic) soils of Sicily during his first Italian journey in 1787 and many other early, qualitative observations have been recorded, the first positive identification of goethite and hematite (by XRD and DTA) in soils was in 1939 by Alexander and coworkers. These authors mentioned lepidocrocite as well, but stated that it had not yet been found in soils. This had to wait until the early fifties when lepidocrocite was described in two redoximorphic soils, one in Holland (Van der Marel, 1951) and the other in England (Brown, 1953). In 1951 Van der Marel also found maghemite in a Dutch soil and explained its formation as a dehydroxylation of FeOOH through fire in the presence of soil organic matter. This mode of formation was again reported by Le Borgne in 1955 and in Germany in 1959 (Schwertmann & Heinemann). After being detected in ochreous deposits from both hot and cold springs by Chukhrov et al. in 1973, ferrihydrite in soils was first documented in 1982 by Schwertmann et al. Pedogenic, bacterial magnetite has been found in a wet soil only recently by Fassbinder et al. (1990) in Germany. Natural schwertmannite has been found in a creek deposit draining a pyrite-contain-

ing rock in Austria (Schwertmann et al., 1995), but not yet in soils, although it may be expected in so-called acid sulphate soils.

However, in the last two decades or so, instrumental techniques for studying nano particles have been developed to such an extent (see Chap. 7) that soil Fe oxides can be identified, quantified and characterized in appreciable detail. These results have especially helped in understanding soil formation (*pedogenesis*) and the behavior of soils towards amendments and pollutants.

16.4.2

Distribution pattern

The distribution pattern of Fe oxides in soils (see Plate 16.I) and in soilscares varies strongly and provides interesting information about the pedogenetic history. In *aerobic* soils, Fe^{2+} ions, once released from a primary mineral, will immediately be oxidized, hydrolysed and immobilized *in situ* (Fig. 16.1). In such a case, the oxides will reflect the Fe distribution in the parent rock and if the latter were evenly distributed, the soils will be homogeneously coloured by Fe oxides (Brown earth; Red earth). Further homogenization is achieved by biotic activity. On the other hand, reactivation by complexation and/or reduction often leads to a redistribution of the Fe oxides within the soil profile during pedogenesis. Remobilization by humics in the topsoil through the formation of soluble Fe-humic-complexes and their migration down the profile where they decompose to form an Fe-oxide enriched B horizon (ortstein) is the classical process of *Podzolization*.

The other mode of remobilization of Fe oxides is biotic reduction in poorly aerated soils by either stagnant surface water caused by a subsoil horizon with a low permeability, or by a high ground water level. In *stagnant water soils* (pseudogleys), the Fe oxides are reduced around roots, both living and dead, where ample biomass is supplied for microbial decomposition (= oxidation) without sufficient O_2 as an electron acceptor. The Fe^{2+} moves away from the roots, is reoxidized and reprecipitates at a higher Eh some distance away. Thereby a bleached, grey zone forms around the root marking the pale colour of the matrix minerals and a strongly coloured zone develops further away from the root with a higher Fe^{III} oxide concentration (Schwertmann & Fitzpatrick, 1992). In addition, ochreous soft mottles and hard spherical concretions (nodules) in pale surroundings characterize such soils.

Ground water soils (Gleys) often consist of a permanently wet, anaerobic lower horizon and an alternately dry and wet upper horizon in which the ground water level fluctuates seasonally. Correspondingly, Fe^{III} oxides in such soils are reduced in the anaerobic subsoil and the Fe^{2+} moves upwards and precipitates as Fe oxide in the horizon of the fluctuating ground water. Such Fe oxide-cemented horizons occur worldwide as bog iron ores, plinthite and lateritic crusts (from *plinthos* Greek; and *later* Latin = brick), all now grouped as *ferricretes* („crete” from concrete). Similarly, in anaerobic, so-called, paddy soils, rice roots supply O_2 from the atmosphere through their aerenchym (gas transport system within the plant) into the rhizosphere and thus precipitate the Fe^{2+} thereby preventing toxification of the plant through high Fe^{2+} concentrations.

In hilly landscapes so-called *soil toposequences* form. They consist of well-drained soils on the slope and groundwater soils in the depression. The iron dynamics clearly reflect this hydrology regime. The colour of a soil and the morphological appearance of the Fe oxides may, therefore, provide a quick and simple assessment of the present and also the past hydrology (Blavet et al. 2000). For example, in such a sequence in the tropical region of Central Brazil, finely dispersed goethite with high Al substitution and Al-hematite predominate in the well-drained soils at the interfluvium and the slope, whereas the groundwater soils of the depression contained cemented, high iron accumulations, so-called plinthites, which are characterized by goethite with low Al-substitution and the absence of hematite (da Motta & Kämpf, 1992).

16.4.3

The various oxides

A generalized overview of the occurrence of the different Fe oxides in various soils (see Schwertmann, 1985) is given in Table 16.2.

16.4.3.1 Goethite

Due to its high thermodynamic stability, goethite is by far the most common Fe oxide in soils. For this reason, soils containing goethite as the sole Fe oxide occur around the globe and predominate in cool to temperate, humid climates. Furthermore, goethite occurs in association with every other common Fe oxide. In warmer regions it is commonly associated with hematite, whereas in cooler climates ferrihydrite and lepidocrocite are frequent partners. Where evenly distributed within the profile and not masked by black humic matter as in many surface soils, goethite imparts a yellow-brown colour (7.5–10 YR) to the soil profile (Plate 16.1 a). It can also be concentrated locally in mottles, concretions, ferricretes and other forms of secondary Fe oxide accumulations.

There are two ways by which goethite can be formed in soils. If iron is released from solid Fe^{II} compounds such as Fe silicates, carbonates and sulphides or, alternatively, from existing Fe^{III} oxides by microbial reduction, the Fe will be oxidized in an

Tab. 16.2 A generalized summary of the occurrence of the different iron oxides in various soils (see Schwertmann, 1985)

Mineral	Major soils
Goethite	Aerobic and anaerobic soils of all regions.
Lepidocrocite	Anaerobic, clayey, non-calcareous soils of cooler and temperate regions.
Ferrihydrite	Groundwater and stagnant water soils (gleys and pseudogleys) and podzols of temperate and cool regions. Paddy soils.
Hematite	Aerobic soils of subtropical, mediterranean and humid to subhumid tropical regions (lateritic and plinthitic soils, red mediterranean soils, oxisols, ultisols). Usually absent in soils of temperate and cool regions.
Maghemite	Aerobic soils of the tropics and subtropics.

aerobic environment either on the spot or after some migration. In the former case the distribution of goethite will mirror the primary Fe distribution of the rocks, whereas in the latter case, it will mirror the aeration pattern of a soil (Plate 16.I) or soilscape. The second pathway involves transformation of ferrihydrite as ferrihydrite is metastable with respect to goethite. This mode of formation is significant where Fe^{2+} ions are quickly oxidized in the presence of crystallization inhibitors which promote ferrihydrite rather than goethite as the primary precipitated phase. With time, ferrihydrite converts to goethite via solution so that the association of goethite with ferrihydrite is common in many post-pleistocene soils. The rate of transformation is not known. As seen from the higher ratios of oxalate to dithionite soluble Fe (see section 16.3), the rate is lower in surface than in subsurface soil horizons due to the retarding effect of humics (Schwertmann, 1966).

16.4.3.2 Hematite and its association with goethite

Hematite, having similar thermodynamic stability to goethite (see chap. 8), is the second most frequent Fe oxide in soils, but, in contrast to goethite, is restricted to soils in warmer, predominantly subtropical and tropical climates. Soils of these zones are often bright red (5YR-10R) because the red colour of hematite masks the yellow of goethite. Hematite very rarely occurs as the sole oxide in a soil, but it is associated with a greater or lesser extent with goethite, often in close association (Fig. 16.2). The ratio $\text{Hm}/(\text{Hm} + \text{Gt})$ varies between 0 and about 0.9–0.95 and this offers the possibility of elucidating the factors which promote hematite as against goethite under soil-forming conditions. Particularly useful in this respect are situations where hematitic (red) soils or soil horizons are associated with non-hematitic, i.e. goethitic (yellow-brown) ones in some systematic way. Such situations exist indeed from the global scale down to the nanometer range.

On a global scale, a line which separates goethitic soils at higher latitudes from hematitic ones at lower latitudes (zonal soil association) can be drawn on both hemispheres. The exact position of this line is not yet known. In the northern hemisphere it is located in Southern China, Southern Europe and the Southern United States

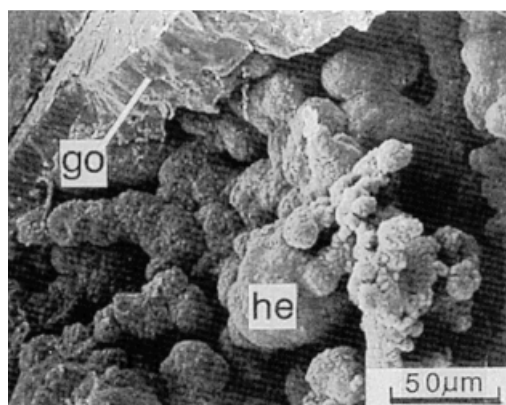


Fig. 16.2 Scanning electron micrograph of an association between goethite (go) and hematite (he) in laterite from Cameroon (Muller, 1987; courtesy J.P. Muller; with permission).

(Schwertmann, 1988b). The zoning is obviously a climatic one (climosequence). Another climosequence occurs in South Brazil (Kämpf & Schwertmann, 1983) and in the Sahelian Niger (Felix-Henningsen, 2000). Climatic gradients are also responsible for red-yellow soil associations at different altitudes above sea level or at different distances from the sea (maritime vs. continental). Examples which have been investigated are the yellow-red soil sequences in the northern foreland of the Alps (Schwertmann et al., 1982a), in Lebanon (Schwertmann, unpubl.), Tasmania (Taylor & Graley, 1967), New Caledonia (Schwertmann & Latham, 1986), and South Brazil (Kämpf & Schwertmann, 1983; Palmieri, 1986; Alexander et al., 1993). In such altitudinal sequences, the cooler and wetter part of the sequence at higher altitude has hematite-free soils, whereas hematitic soils prevail in the drier and warmer part at lower altitude so that the ratio $Hm/(Hm+Gt)$ falls as the temperature decreases and the rainfall increases. For example, in South Brazil the ratio decreases from 0.79 to 0 over a distance of 450–600 km W $\Rightarrow$ E as the mean annual temperature decreases from 20 °C to 14 °C and the annual rainfall increases from 140 cm to 250 cm.

Hematitic-goethitic soil associations on a smaller scale are formed in so-called *toposequences*, i.e. soils along a topographic transect under an identical macroclimate (intrazonal soil associations). Provided the macroclimate allows hematite formation, red soils often occur on the drier slopes and grade into yellow soils in the wetter depressions (Fig. 16.3). Such toposequences are very common in tropical regions. Examples from Brazil (Curi & Franzmeier, 1984a; Santana, 1984; da Motta & Kämpf, 1992) and Malawi (Karim & Adams, 1984) have been reported. The so-called dry-edge effect in the coastal plain of North Carolina where red soils occupy the dry edge of a valley and the yellow soils the wet plateau is another example caused by a topography-dependent water regime (Daniels et al., 1975). A similar situation occurs in Queensland, Australia (Coventry et al., 1983). Although the macro climate within each of these toposequences is the same, the climate within the soil (pedoclimate) varies, mainly because of differences in hydrology. Blavet et al. (2000) were able to link the present water regime, i.e. the annual rate of water logging in a soil toposequence from Togo with the redness of the soils (most likely reflecting the hematite/goethite ratio). This demonstrates that soil colour can be taken as an indication of long-term soil hydrology. In a chronosequence of soils on Pleistocene sediments from the Blue Ridge Mountains, USA, the B horizon became redder with age, probably due to the fact that the older soils had experienced warmer periods in interglacial times (Leigh, 1996). Two more examples of different $Hm/(Gt + Hm)$ ratios in neighbouring soils are hematitic soils on high-Fe mafic rocks vs. hematite-free soils on low-Fe felsic rocks and terra rossa-rendzina pairs on hard vs. soft limestones (Singer et al. 1998), respectively.

The effect of the position of a soil within a toposequence on the type of Fe-oxide is also used in interpreting fossil soils on the ancient Gondwana surfaces (Africa, South America, Australia). Such (paleo-)soils often consist of three parts, resting on the unweathered rock, viz. (from bottom to top) saprolite ("dead" rock), mottled zone and ferricrete, along which the Fe oxide concentration usually increases substantially. The very high absolute concentration of goethite in the ferricretes in higher positions of the present landscape (mesas) and its low Al substitution (Zeese et al.

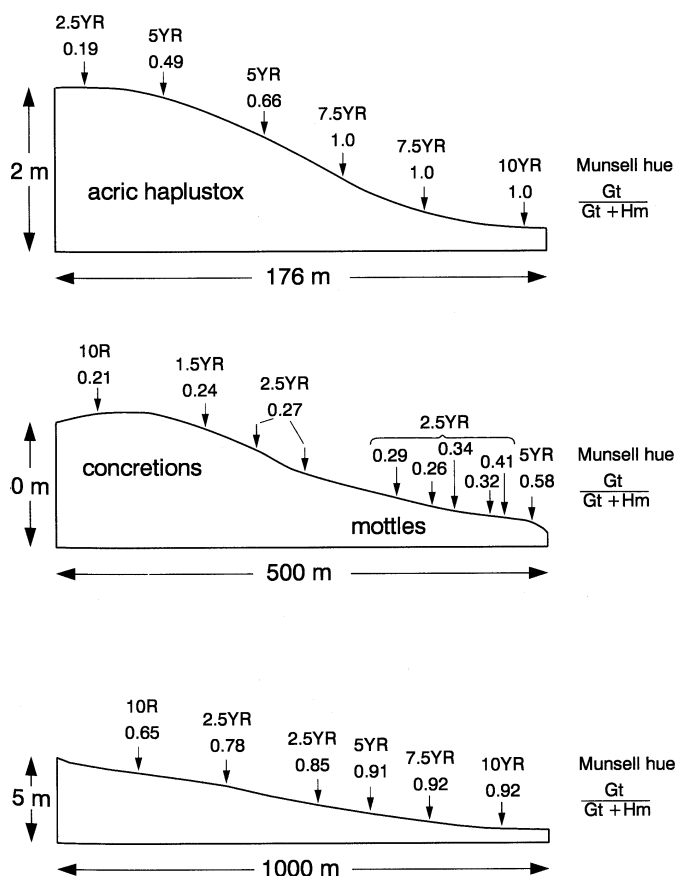


Fig. 16.3 Munsell colour notation and goethite/(goethite + hematite) ratio $[Gt/(Gt+Hm)]$ in three soil toposequences, two from Brazil (upper & middle) and one from Malawi (lower) (Data from Curi & Franzmeier, 1984 a; Santana, 1984; Karim & Adams, 1984; with permission).

1994, Horvath et al. 2000), suggests that these ferricretes have actually formed in former lowlands under phreatic and redoximorphic conditions. The presence of reduced (trivalent) vanadium in goethite also points in this direction (Schwertmann & Pfab, 1996). Later these soils have come into an upland position by preferential erosion of the former upland soils because of climatic changes and, possibly, tectonic activity (so-called relief inversion). Goethite was also the dominant form associated with younger Fe oxide formation in the lower part of the present landscape in contrast to the hematitic ferricretes on the higher terrace or plateau position, e.g. as described in Niger (Bui et al. 1990).

On even smaller scales, one can also find differentiation between goethite and hematite within a *soil profile*. Often, yellow, hematite-free toposoils are underlain by red

hematitic subsoils. In Minas Gerais, Brazil, Muggler et al. (2001) identified hematite with low Al-substitution ($<0.1 \text{ mol mol}^{-1}$) with uniform MCL_a of ca. 20–30 nm in the (older) saprolite at depth, overlain by a soil containing younger, highly Al-substituted goethite, and suggest that the latter formed from the former. Indeed, yellow topsoils over red subsoils are very common in the tropics, but have been explained, not by transformation, but by preferential dissolution of the primary hematite; this can be simulated in the laboratory (see chap. 12).

All these observations stress the fact that the oxide forming conditions at different depths within a soil profile differ with respect to biotic activity, organic matter content, pH, Eh, hydrology etc. and also varied during pedogenesis. The information stored in iron oxide analysis, therefore, helps in unravelling the polygenetic history of older soils. Primary differentiation of the two oxides according to the different formation conditions is probably the main process leading to the widely varying goethite/hematite ratios on different scales. With respect to later conversion from hematite to goethite or vice versa, reductive dissolution and reprecipitation is considered to be much more likely than transformation by solid-state de- or rehydration.

The following scheme summarizes the environments of formation on different scales:

<i>Goethite</i>		<i>Hematite</i>
	Macro	
Higher latitude		Lower latitude
	S	
Humid rain forest without dry periods		Savannah with dry periods
	C	
Lower parts of a toposequence		Upper parts of a toposequence
	A	
Topsoils		Subsoils
	L	
Low Fe (acid) rocks, soft limestones		High-Fe (basic) rocks, hard limestones
	E	
	Micro	

The observed hematite/goethite associations in soils can still be only partly explained. Considering the very similar thermodynamic stability of both oxides, the differentiation is difficult to explain if equilibrium is assumed. As described in Chapter 8, three factors must be taken into account for thermodynamic model calculations: water activity, crystal size and Al substitution. Calculations by Tardy and Nahon (1985) and by Trolard and Tardy (1987) have predicted that lowering of the water activity below unity, as in very small pores, should favour hematite (Michalet et al., 1993), and increasing Al in the system should favour goethite. The effect of particle size is shown in Figure 8.3 based on the calculations of Langmuir (1971). No general validation of these model calculations has so far been produced in *in vitro* or *in situ* studies.

On the other hand, in a non-equilibrium situation, kinetic factors play a key role. Information about the mechanisms of formation (see Chap. 13 & 14) may then be of

some assistance. In this context it is relevant that ferrihydrite is, as generally agreed, a necessary precursor of hematite at least under the conditions of soil formation. Hence, factors which promote ferrihydrite formation and its transformation to hematite rather than goethite will, at the same time, explain preferential hematite formation.

In applying these principles to soils, drier and warmer pedoenvironments such as those in lower latitudes, at lower altitudes and higher slope positions are expected to promote hematite formation because they favour the transformation of ferrihydrite to hematite (rather than that of goethite). Torrent and Cabedo (1986) have postulated that in Mediterranean soils, Fe release and ferrihydrite formation may take place during the wet, cool winter followed by transformation of ferrihydrite to hematite during the dry and warm summer. Water activity measurements with tensiometers in several rendzina/terra rossa soil pairs in Israel support this concept (Singer et al. 1998): more hematite was present in the drier terra rossa on hard limestone than in the rendzinas on soft chalk. The effect of organic matter, a specific one in surface soils, is due to its ability to complex Fe. Organics thereby prevent the (higher) solubility product of ferrihydrite from being exceeded but not that (lower) of goethite. This effect may suppress hematite formation in top soils, but not in subsoils. Redder B horizons were found in Columbian soils with less organic matter (Lips & Duivenvoorden, 1996). Hematitic soils on rocks rich in Fe (such as basic igneous rocks) versus neighbouring hematite-free soils on low-Fe rocks (e.g. sediments) may be explained similarly by assuming that ferrihydrite and thus hematite only form if the rate of release of Fe from the parent rock is relatively high. A pH effect similar to that found in synthesis experiments (see Chap. 13) has also been documented for soils in southern Brazil (Kämpf & Schwertmann, 1983).

The laboratory derived model of hematite formation in soils via ferrihydrite has received general acceptance. So far, it is the only way to produce hematite at ambient temperatures and in the pH range of soils. Support from soil analysis, however, is meagre. Hematite is usually associated with other Fe oxides, mainly with goethite but not with ferrihydrite. There seems to be only one report of a ferrihydrite-hematite association (based on XRD and Mössbauer spectra) viz. in several andisols formed from basalt in the warm and moist climate of Hawaii (Parfitt et al., 1988). In this case, in addition to the low age of the soils, high release of Si may retard the transformation of ferrihydrite to hematite, whereas normally, the rate of transformation of ferrihydrite seems to be higher than that of ferrihydrite formation, so that this mineral does not persist.

Another possible explanation for the yellow (goethitic) top soil over a red subsoil situation is the change in pedoclimate from a drier to a moister one during the pedologic history. The damper environment has led to preferential reductive dissolution of hematite in the surface soil by microbial activity leaving behind a yellow soil containing only goethite (Schwertmann, 1971); this process is called *xanthization* (yellowing). This explanation has been backed by laboratory (see Chap. 12) and soil studies both of which showed that reduction of hematite was faster than that of goethite (Torrent et al., 1987; Macedo & Bryant, 1989; Fontes & Weed, 1991; Jeanroy et al., 1991; Smeck et al., 1994) unless the hematite is trapped within kaolinite aggregates

(Malengreau et al., 1996). This process was followed in the laboratory by reducing a tropical red soil with dithionite. Not only was the hematite dissolved preferentially, but also the goethite was more resistant the higher its Al-substitution. This suggests that structural Al is at least part of the reason for the greater resistance of goethite to reductive dissolution (Peterschmitt et al., 1996), in agreement with studies on synthetic Al-goethites (see chap. 12). In other words, xanthization is not due to the hematite goethite transformation, but to preferential dissolution of hematite in a hematite-goethite containing soil.

16.4.3.3 Lepidocrocite, feroxyhyte and green rust

Lepidocrocite is much less common in soils than goethite and hematite, although it is not rare. It has been identified under quite different macroclimatic conditions in many soils around the world (Van der Marel, 1951; Brown, 1953; Schwertmann, 1959b; Schwertmann & Fitzpatrick, 1977; Schwertmann & Taylor, 1979; Kämpf & Schwertmann, 1983a; Adams & Kassim, 1984; Fitzpatrick et al., 1985; dos Anjos et al., 1995). Common to most of its occurrences are redoxomorphic environments, i.e. a seasonal alternation of reducing and oxidizing conditions. Anaerobiosis during the wet season leads to the formation of Fe^{2+} which then moves into oxygenated zones where lepidocrocite precipitates and forms mottles, bands or concretions. If lepidocrocite predominates in these zones, it can be recognized by its typical orange colour (see Chap. 6). Lepidocrocite, therefore, indicates the temporary formation of Fe^{2+} ions. In Ultisols on Neogene sediments in East Kalimantan, the concentration of lepidocrocite in the downslope members of the toposequences was inversely related to the amount of exchangeable Al (Ohta et al., 1993). This is in agreement with synthesis experiments which show that Al suppresses lepidocrocite. Lepidocrocite is also suppressed by higher carbonate concentration in solution, so that it is not found in calcareous soils.

In non-calcareous soils, however, lepidocrocite is often associated with goethite. A typical association on a microscale was found in an Fe oxide concentration around roots, a so-called rhizoconcretion or pipe stem. It was suggested that the predominance of goethite close to the root is due to a higher partial pressure of CO_2 in the rhizosphere, whereas further away from the root, lepidocrocite was the main FeOOH phase (Schwertmann & Fitzpatrick, 1977). Goethite and lepidocrocite in intimate association have also been found around rice roots (Chen et al., 1980; Wang et al., 1993; Golden et al. 1997). The goethite promoting effect of carbonate ions during Fe^{2+} oxidation is in accordance with *in vitro* experiments (see Chap. 13). The formation of these two minerals by two competitive reactions has also been illustrated by an inverse relationship found between the concentration of the two FeOOH forms in soils of East Kalimantan (Fig. 16.4) (Ohta et al., 1993).

As lepidocrocite is metastable relative to goethite, it can be expected that lepidocrocite may transform into goethite. As demonstrated in the laboratory, this transformation proceeds via solution (see Chap. 14). Electron micrographs from a redoxomorphic soil in Australia indicate that the same process seems to occur in soils (Fig. 16.5). The lepidocrocite crystals show dissolution features and there are small, acicular, goethite crystals in their neighbourhood. *Feroxyhyte* was reported in two allopha-

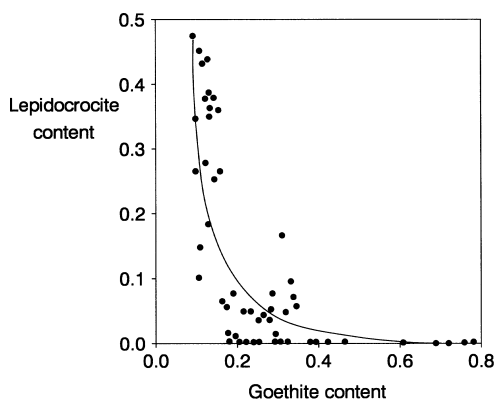


Fig. 16.4 Inverse relationship between the relative lepidocrocite and goethite content in soils of Kalimantan (Ohta et al., 1993; with permission).

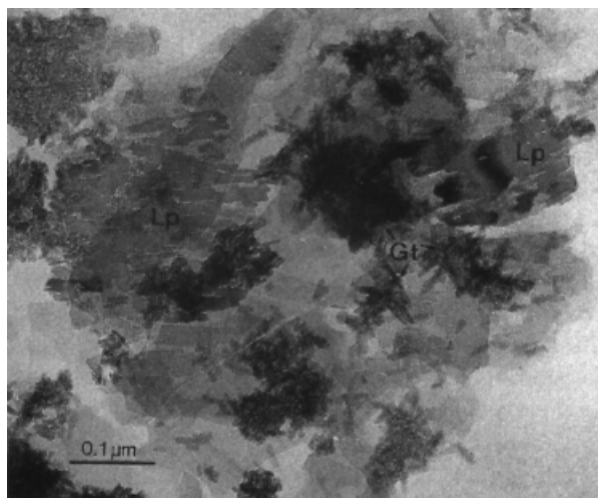


Fig. 16.5 Electron micrographs of an association of lepidocrocite (Lp) with goethite (Gt) from a redoximorphic soil, Natal, South Africa (courtesy P. Self).

nic soils in Hawaii (Udands) which had formed from basalt under conditions of high rainfall ($3.0\text{--}3.8\text{ m a}^{-1}$) (Parfitt et al., 1988). A *green rust* phase, presumably with OH in the interlayer position, has been identified under temporarily anoxic conditions in three redoximorphic soils in France. It causes the green-blue colour of the horizon (5BG 6/1) and oxidizes rapidly on exposure to air changing to a 2.5Y 5/6 colour (Trolard et al., 1997; Bourrie et al., 1999). The name *fougerite* has been suggested for this phase.

16.4.3.4 Ferrihydrite and its association with goethite

Due to its metastable nature, ferrihydrite can only be expected in relatively young (Holocene) soils or in those in which its transformation to more stable oxides is in-

hibited or retarded. Ferrihydrite is often associated with goethite, whereas an association with hematite, although expected from synthesis experiments, has not been found in soils. The occurrence and properties of ferrihydrite in soils and related environments were summarized by Childs (1992). Childs and coworkers identified ferrihydrite by XRD, Mössbauer spectroscopy and IR in young soils on volcanic rocks (Andosols) in Tonga (Childs and Wilson, 1983), New Zealand (Childs et al. 1990) and in Japan (Childs et al., 1991). The lower limit of detection by differential XRD (DXRD) was around 50 to 100 g kg⁻¹. In a sequence of soils on lava flows (Azores) with ages of between ca. 500 and 5000 yr, decreasing Fe_o/Fe_d values (0.86; 0.62; 0.51 and 0.25) may be taken as corresponding to a gradual disappearance of the metastable ferrihydrite in favour of goethite and/or hematite as the soils become older (Malucelli et al. 1999). Accumulation of ferrihydrite was also anticipated in the B horizon of a 240 yr old Spodosol on a moraine in SE-Alaska (Alexander and Burt, 1996).

A pedogenic environment prone to ferrihydrite formation also prevails in groundwater soils (Gleys) of the glaciated area of NW Europe; here, large amounts of Fe oxides accumulated during the Holocene era as so-called bog iron at the boundary between the permanently reduced subsoil and the oxidized horizon where the groundwater level fluctuates seasonally. Due to the very high Fe oxide content of 0.2–0.8 g g⁻¹, ferrihydrite could be identified by DXRD and Mössbauer spectroscopy (Schwertmann et al., 1982). Siliceous 2-line-ferrihydrite (0.5 g g⁻¹ Fe; 60 mg g⁻¹ Si) was also identified in artificial water channels (races) of paddy fields in Japan as a young oxidation product of Fe²⁺ which is produced under the anoxic conditions in the paddy soil (Childs et al., 1990).

The rapid oxidation of Fe²⁺ close to the surface and in the presence of a fair supply of organic matter and dissolved Si, conditions which hinder crystallization, leads to ferrihydrite instead of goethite. The ferrihydrite is, however, often associated with goethite and it is still unknown whether the two minerals have formed simultaneously or in sequence. Simultaneous formation seems more likely for two reasons: in the first place, low-temperature hydrolysis of Fe³⁺ or oxidation of Fe²⁺, both, led to mixtures of the two oxides in different proportions if the rate of hydrolysis/oxidation was varied (Schwertmann et al. 1999; Schwertmann & Cornell, 2000). Secondly, the transformation of ferrihydrite, especially in the presence of Si, appears to be extremely sluggish.

Another group of soils in which ferrihydrite has been identified are *podzols* (Spodosols) (Goodman & Berrow, 1976; McBride et al., 1983; Schwertmann & Murad, 1990a). In brief, podzolization is a process in which primary Fe oxides are remobilized by chelating humic compounds which then migrate downwards into the subsoil. Here they are reprecipitated to form eventually, a cemented B horizon (Ortstein) relatively enriched in Fe together with carbon, Al and Si. Application of organic matter (peat, spruce litter) to the surface of such soils has been shown to induce Fe migration and B-horizon formation within several decades (Cunningham et al. 2001). Because the absolute Fe concentration is not very high (5–20 g kg⁻¹), ferrihydrite could only be identified (in agreement with a Fe_o/Fe_d close to 1) by Mössbauer spectroscopy. Besides ferrihydrite, Fe-humic complexes also exist in these horizons (Evans & Wilson, 1985; Schwertmann & Murad, 1988). Much higher Fe concentra-

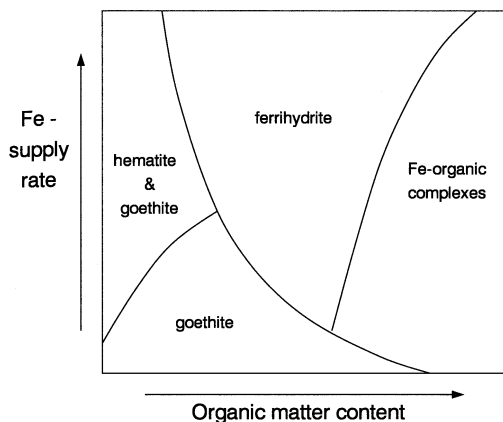


Fig. 16.6 Tentative schematic representation of the effect of organic matter content and rate of Fe supply on the formation of various Fe forms in soils (Schwertmann et al., 1986; with permission).

tions ($200\text{--}300\text{ g kg}^{-1}$) occur in podzols with thin, hardened iron bands (placic horizons) with Fe_o/Fe_d ratios of $0.4\text{--}0.9$ indicating that ferrihydrite is associated with the better crystalline Fe oxides, goethite and lepidocrocite (Stahr, 1972; Campbell & Schwertmann, 1984). The latter authors found a linear relationship between the intensity of the (110) XRD peak of ferrihydrite at $\sim 0.25\text{ nm}$ and Fe_o ($r = 0.98$; $n = 15$). In a range of andisols formed from basalt on Hawaii, the amount of ferrihydrite (based on XRD and Mössbauer spectra) increased with increasing mean annual precipitation ($1.0\text{--}3.8\text{ m a}^{-1}$). It was suggested that its formation was induced by the high rate of Si release from the rock (Parfitt et al., 1988).

In summary, both a high rate of Fe^{II} oxidation and the presence of silicate and organics such as humics, promote ferrihydrite formation because these factors impede the formation of crystalline Fe oxides. This is depicted schematically in Figure 16.6. With low organic matter content, hematite and goethite are favoured, whereas increasing amounts of organic matter lead to goethite when Fe supply is low and to ferrihydrite when Fe supply is higher (Schwertmann, 1966; Schwertmann et al., 1986). With very high organic matter content, all Fe is organically complexed and no oxides form (Goodman & Cheshire, 1987; Schwertmann & Murad, 1988).

16.4.3.5 Magnetite and maghemite

The magnetic properties of soils are often characterized by a maximum in magnetic susceptibility in the top soil which suggests pedogenic formation of the ferrimagnetic Fe oxides, magnetite and/or maghemite. As seen from the widespread occurrence of magnetite in biota, especially in so-called magnetotactic bacteria (see Chap. 17), the formation of these ferrimagnetic oxides under ambient conditions, e.g. in soils, seems feasible. A convenient way of detecting ferrimagnetic minerals in soils is to measure the magnetic mass susceptibility (see Chap. 7).

Lithogenic *magnetite* is a common mineral in the coarse, heavy mineral fraction of soils. In contrast, pedogenic magnetite has been discovered only very recently. Both an abiotic (Maher & Taylor, 1988) and a biotic (Fassbinder et al., 1990) route have been suggested. The latter authors identified magnetite by its unit cell edge length

of $a = 0.8408(3)$ nm and by its Curie temperature of 580–600 °C, both parameters being different from those of maghemite. The idiomorphic crystals had an octagonal, hexagonal or prismatic outline and were between 10 and 100 nm across which covers the single domain to superparamagnetic size range. This and their association into chains within bacterial cells indicated biogenic formation as a result of biotically controlled biomineralization in soils (Fassbinder et al., 1990). The absence of this spatial arrangement led Maher and Taylor (1988) to favour inorganic neoformation, possibly biologically induced by a reaction between microbially-produced Fe^{2+} and a reactive Fe oxide such as ferrihydrite (Taylor & Schwertmann, 1974). Auerswald et al. (2001) identified pedogenic magnetite in a wetland soil of Israel by Mössbauer spectroscopy and suggested formation by fire under reducing condition.

Maghemite is widespread in soils in tropical and subtropical regions. It may be distributed throughout the soil profile or accumulated in the surface soil (Le Borgne, 1955; Singer & Fine, 1989). It may also be dispersed in the matrix or concentrated in concretions. It is a common constituent of tropical soils from basic igneous rocks (Schwertmann and Latham, 1986; Fontes & Weed, 1991; Goulart et al., 1998; Da Costa et al., 1999), but is also widespread in soils from acid rocks (Taylor & Schwertmann, 1974, 1974a). Crystal size, as measured by XRD line width, was found to be mostly in the range of 10 to 40 nm (N.Sabil, unpubl.). Soil maghemites are, therefore, often in the superparamagnetic (<20 nm) or single domain (20–40 nm) range and may be quantified by the magnetic susceptibility: for example, a linear correlation ($r^2 = 0.89$) between the maghemite content (by XRD) and the mass specific magnetic susceptibility χ was found for 42 maghemite-containing samples <2 μm in size from soils on basaltic andesite in southern Brazil (Da Costa et al., 1999).

Two different pathways of formation are possible (Stanjek, 2000). One route involves aerial oxidation of lithogenic magnetite as suggested for Brazilian Oxisols on basic igneous rocks. The mechanism of this topotactic reaction is described in Chapter 14. These maghemites are usually titaniferous as are the magnetites from which they are derived (see Chap. 15) and almost free from or very low in Al (Allan et al., 1989). Their unit cell size is a function of the residual Fe^{II} and the Ti content. A range of unit cell sizes can, therefore, be observed. An example of the composition of a completely oxidized, titanous magnetite from a soil is $[\text{Fe}_{0.29}\text{Al}_{0.08}] \{\text{Fe}_{1.43}\text{Ti}_{0.18}\text{O}_{0.39}\}\text{O}_4$ ([] = tetrahedral site; { } = octahedral site; ■ = vacancy) (Goulart et al. 1998). In agreement with synthesis experiments (Feitknecht, 1965) (see Chap. 14), smaller magnetite crystals transform to maghemite, whereas larger ($\approx \text{mm}$) ones oxidize pseudomorphologically to hematite (so-called martitization) (Anand & Gilkes, 1984). In contrast, clay sized maghemites in soils on basic igneous rocks may well be Al-substituted (e.g. 0.05–0.16 mol mol⁻¹), and this may indicate that they form via solution in an Al-containing environment rather than by solid-state transformation (Da Costa et al., 1999).

The second possible route for maghemite formation in soils involves heating lepidocrocite at ~ 250 °C (see Chap. 14). Such a case has been reported for a burnt, lepidocrocite containing layer in a peat deposit (Schwertmann & Heinemann, 1959). Lepidocrocite is, however, not a widespread mineral in those soils in which maghemite is common. Goethite (or ferrihydrite), however, also converts to maghemite (rather

than to hematite) by heating, if organic matter is present and does not oxidize before the goethite dehydroxylates. This is often the case in soils covered by vegetation and with limited air access when the vegetation is set on fire. Because fires are common in tropical and subtropical regions, maghemite is widespread in the soils. The close positive relationship between its abundance and that of corundum ($\alpha\text{-Al}_2\text{O}_3$) is a further proof of the higher temperatures experienced by such soils because corundum is clearly a product of heating Al compounds (Anand & Gilkes, 1987b). Furthermore, the Al-for-Fe substitution in such maghemite as seen from the reduced unit cell size (see Chap. 3), confirms that Al-goethite is the precursor (Schwertmann & Fechter, 1984); lithogenic magnetites are usually low in or free from Al. Al-substituted soil maghemites had a reduced unit cell edge length of 0.832 nm indicating an Al/(Fe + Al) ratio of ca. 0.15 mol mol⁻¹. The temperature required for the transformation increases with increasing Al substitution.

In addition to its widespread occurrence in tropical areas, localized deposits of maghemite have also been found in temperate regions such as The Netherlands (Van der Marel, 1951), Germany (Schwertmann & Heinemann, 1959; Stanjek, 2001), California (Singer & Fine, 1989) and Denmark (Noernberg et al. 2002) where the presence of charcoal indicates association with fires; hematite as a product of heating is also commonly present. Stanjek (2000) demonstrated by structural analysis using Rietveld fitting of XRD patterns, that maghemites formed by heating of FeOOH polymorphs, contain structural OH compensating for Fe vacant sites in the structure.

Because maghemite is a ferrimagnetic phase, small concentrations increase the magnetism, e.g. the magnetic susceptibility χ (chap. 6) of soils noticeably even when the concentration is still below the detection limits of XRD. A large number of such measurements has been made and there have been attempts to correlate this with a number of factors (e.g. climate, age of soil, magnetism of parent rock, Fe content of soil) (Singer et al., 1996). In the topsoil of 120 profiles of subtropical China, a significant correlation was observed between magnetic susceptibility and Fe_d (Shenggao, 2000). Buried soils (paleosols) within a deep loess profile of China showed higher susceptibilities wherever soil formation in a warmer climate between two loess sedimentation periods had taken place (Vandenberghe et al., 1997). In three soil catenas of Saskatchewan on glacial till, χ decreased downslope and was negatively correlated with the Fe_o/Fe_d ratio and positively with the amount of sand. The latter effect is explained by the presence of lithogenic magnetite inherited from the till (De Jong et al. 2000).

16.5

Properties

16.5.1

Surface area, crystal morphology and size

Because Fe oxides are intimately associated with other soil components, it is not easy to determine the specific surface area of soil Fe oxides. An approximation can be obtained by attributing the surface area difference from before and after selective re-

removal of Fe oxides, to the Fe oxides. The amount of Fe oxide can be estimated from the weight loss, although some other constituents are also dissolved, especially in allophanic soils. The factor between Fe_d and Fe oxides is about 2. With these procedures, areas of between 45 and $110 \text{ m}^2 \text{ g}^{-1}$ of Fe oxides were obtained for 13 Brazilian Oxisols containing goethite and hematite (Fontes and Weed, 1996).

The crystals of soil Fe oxides are usually less well developed than those of synthetic ones. Goethite crystals from soils are, like synthetic ones, acicular (Fig. 16.7 a, e) and show defects, micropores and serrated edges. Stars composed of spindles (Fig. 16.7 b)

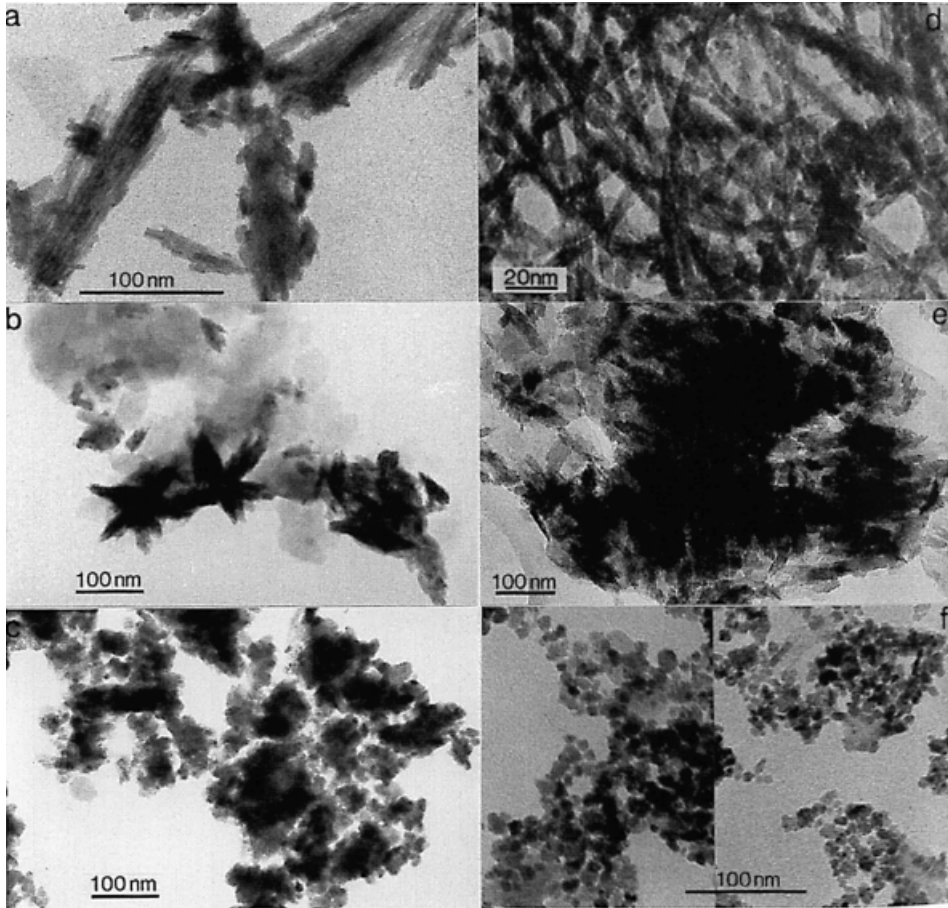


Fig. 16.7 Electron micrographs of soil goethites. a) Acicular crystals from an Oxisol on peridotite, New Caledonia (Schwertmann & Latham, 1986; with permission). b) Starlike crystals from a redoximorphic paddy soil, China. c) Irregular crystals from an Ultisol on basalt, South Brazil (see also Schwertmann & Kämpf,

1983). d) Fibrous crystals from a podzol, Scotland (Nakai & Yoshinaga, 1980; with permission). e) Small acicular crystals from a redoximorphic soil, Natal, South Africa (courtesy P. Self). f) Equidimensional crystals from an Oxisol, Brazil (Fontes et al., 1992; courtesy M.R. Fontes; with permission).

have been found in redoximorphic soils and fibrous crystals, 5 nm wide, in podzols (Fig. 16.7d) (Nakai & Yoshinaga, 1980; Fordham et al., 1984). Often, however, the conditions for crystal growth are so poor that no specific morphology develops (Fig. 16.7f) and irregular particles predominate (Fig. 16.7c) (Kitagawa, 1983). It is, therefore, often not possible to identify soil goethite by its crystal morphology. A similar situation exists for soil hematites. Platyness is poorly expressed and if subrounded (Fig. 16.8a, b), hematite particles can no longer be distinguished from subrounded goethites. Some soil hematites show a grainy structure (Fig. 16.8c) like synthetic ones which have been formed from ferrihydrite aggregates, which provides support for a similar mode of formation (Schwertmann et al. 2000). These grainy crystals seem to scatter X-rays coherently, i.e. they act like single crystals which is also in agreement with their

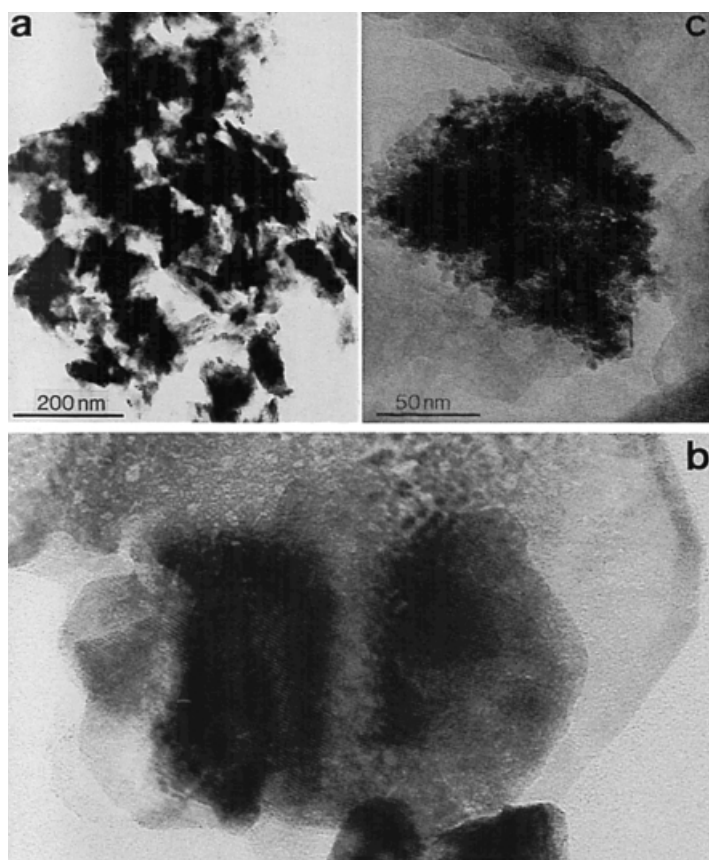


Fig. 16.8 Electron micrographs of soil hematites. a) Irregular crystals from a laterite, Nigeria, after NaOH treatment to remove kaolinite (see Torrent et al., 1994; with permission). b) same as a): crystals on a silicate flake. See lattice

fringes of ca. 1.4 nm, corresponding to the *c* edge length on the lower left side (courtesy J. Torrent) c) Grainy crystal from an Ultisol, South Brazil (Kämpf & Schwertmann, 1983; with permission).

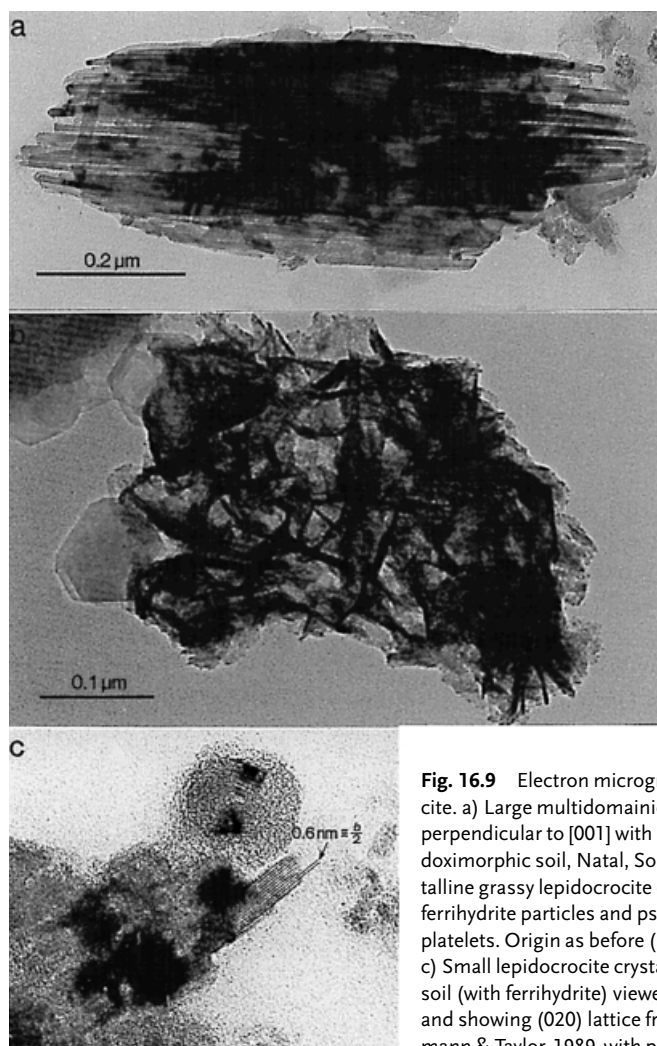


Fig. 16.9 Electron micrographs of soil lepidocrocite. a) Large multidomainic lath-like crystal viewed perpendicular to $[001]$ with laminar pores from a redoximorphic soil, Natal, South Africa. b) Poorly crystalline grassy lepidocrocite crystals mixed with tiny ferrihydrite particles and pseudo-hexagonal kaolinite platelets. Origin as before (a & b: courtesy P. Self). c) Small lepidocrocite crystal from a hydromorphic soil (with ferrihydrite) viewed perpendicular to $[001]$ and showing (020) lattice fringes (see also Schwertmann & Taylor, 1989, with permission).

surface area. Soil lepidocrocite crystals appear as thin laths which are highly serrated (multidomainic) at their terminal ends (Fig. 16.9a). They are very similar to their synthetic counterparts when the latter are produced under ambient conditions by oxidation of Fe^{II} solutions. Smaller crystals appear as needles (Fig. 16.9b); they can be viewed perpendicular to $[001]$ and show (020) lattice fringes (Fig. 16.9c).

The crystal size of soil Fe oxides usually ranges from a few to several hundred nm. A survey of 256 goethites, 101 hematites and 72 lepidocrocites from soils around the world showed maxima in the mean coherent length (MCL) perpendicular to (101), of 15–20 nm for goethite and ca. 40 nm perpendicular to (110), for hematite (Fig. 16.10). These values have been deduced from XRD line broadening using the Scherrer for-

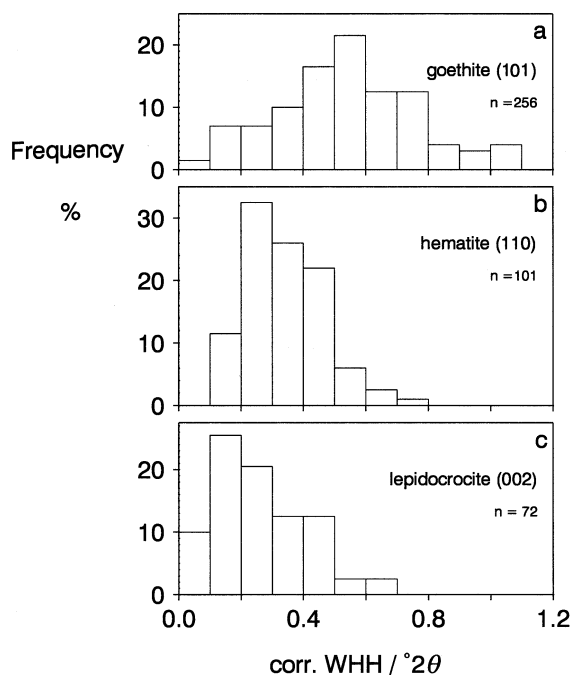


Fig. 16.10 Frequency distribution of the corrected width at half height (WHH) of goethites (101), hematites (110) and lepidocrocites (002) from soils and other surface environments. The range of WHH at the abscissa corresponds to about 10–100 nm (Schwertmann, 1988 b; with permission).

mula (see Chap. 4) and assuming that the width is due solely to particle size broadening. It seems to be the rule that hematite crystals have a higher MCL than the co-existing goethites (Zeese et al., 1994; Prasetyo & Gilkes, 1994). For goethites and hematites from Western Australian lateritic soils and duricrusts (64 samples), the following results have been obtained: MCL_{111} of goethites 13–26 nm, MCL_{104} and MCL_{110} of hematites 30–42 and 14–52 nm, respectively (Anand & Gilkes, 1987; 1987 a). The platy nature of soil hematite crystals can be recognized by MCL_{110} being higher than MCL_{104} because MCL_{110} reflects the size of the plate and MCL_{104} reflects its thickness. Lepidocrocites seem to form larger overall crystals (Fig. 16.10), even in the [010] direction which represents the plate thickness. It is suggested that slow oxidation of Fe^{2+} ions within the soil matrix causes these relatively large crystals to form, whereas lepidocrocite in the pores was less well crystalline due to better access of air and, thus, faster oxidation (Schwertmann, 1988).

16.5.2

Aluminium substitution

The omnipresence of aluminium in weathering environments results in most of the Fe oxides in soils, except lepidocrocite, being Al-substituted. The possible range of substitution as deduced from synthesis experiments (see Chap. 3) viz. up to $Al/(Fe + Al)$ of ca. 0.33 in goethite and up to $Al/(Fe + Al)$ of ca. 0.16 in hematite is also found in soil goethites and hematites. Where the two oxides coexist on a small scale

(mm to cm), goethite always has more Al in the structure than does hematite, indicating that Al goes preferentially into goethite (Fontes & Weed, 1991; Fontes et al., 1991; Prasetyo & Gilkes, 1994). Goethite has been found to contain about twice as much Al as hematite in some cases (Schwertmann & Kämpf, 1984; Singh & Gilkes, 1992; Da Motta & Kämpf, 1992), but no correlation has been found in others (Anand & Gilkes, 1987; Zeese et al., 1994). The ratio may depend on whether or not the two oxides were formed simultaneously in the same environment. Maghemites from tropical soils contained Al up to an Al/(Fe + Al) ratio of ca. 0.15 as indicated by chemical analysis and reduction in unit cell size (Schwertmann & Fechter, 1984; Fontes & Weed, 1991).

In addition to those for synthetic goethites and maghemites, linear relationships between Al substitution and unit cell parameters have also been found for natural maghemites (Schwertmann & Fechter, 1984) and goethites. As seen from Table 16.3, the relationship for goethite may differ for goethites from different natural environments. Those from tropical soils showed a higher diminution of the unit cell than those from lake iron ores formed in a cool, humid area (Finland) or from Fe oxide bands in Galicia, Spain (Barral Silva & Guitian Rivera, 1987). This may reflect different conditions of formation (Schwertmann & Carlson, 1994) leading to a variation in properties other than Al substitution which – as for example extra OH (see chap. 2) – affect the unit cell parameters. A systematic study of goethites from temperate soils is not yet available, nor has the relationship between the extent of Al substitution and the unit cell parameters of soil hematites been established, because it is not possible to partition the Al between goethite and hematite by chemical methods.

Owing to their extremely low solubilities in an aerobic environment, goethite and hematite remain unchanged over geological time spans. They may, therefore, store information about the environment in which they formed. Al substitution may be one such piece of information. Thus, medium to high Al substitution has been observed in goethites from tropical and subtropical soils, bauxites and saprolites (Fitzpatrick & Schwertmann, 1982; Schwertmann & Kämpf, 1983; Curi & Franzmeier, 1984, 1984a; Anand & Gilkes, 1987; Muller & Bocquier, 1987; Fontes & Weed, 1991; Fontes et al., 1992). In these highly weathered soils, Al-goethites form in immediate contact with Al sources such as feldspars, micas, kaolinite and gibbsite which may explain their high Al substitution. An exception is goethite formed from ultramafic rocks low in Al such as peridotite (Schwertmann & Latham, 1986). Goethite with

Tab. 16.3 Linear correlation between the unit-cell parameter *b* and the chemically determined Al substitution of goethites from soils, sands and lake ores

Sample group	<i>n</i>	Range of substitution mol mol ⁻¹	Intercept nm	Slope nm	<i>r</i> ²	Reference
Tropical soils [§]	84	0.01–0.32	0.3026(3)	–0.00207(5)	0.962	Schwertmann & Carlson, 1994
Fe-oxide accumulations in sands, Spain	50	0–0.23	0.3024	–0.00124	0.889	Barral Silva & Rivera, 1987
Lake ores, Finland	30	0.02–0.19	0.3020(2)	–0.00090(6)	0.897	Schwertmann & Carlson, 1994

low substitution commonly prevails in weakly acid soils or in goethite accumulations in redoximorphic soils (Fitzpatrick & Schwertmann, 1982; Schwertmann et al., 1987; Zeese et al., 1994). It is believed that under these conditions, goethite forms by oxidation of Fe^{II} in an environment either low in soluble Al or away from the immediate vicinity of solid Al sources (e.g. in larger pores). In laterites, the intimate co-existence of goethites with two very different levels of Al substitution may then indicate two different (subsequent) environments (Tardy and Nahon, 1985; Malengreau et al. 1997).

Variations in the level of Al substitution of goethite have also been observed within a soil profile. In deep Oxisols in the Cameroons, Muller and Bocquier (1987) found values for $\text{Al}/(\text{Fe} + \text{Al})$ of 0.07–0.15 mol mol⁻¹ in goethites from ferruginous nodules, of 0.13–0.20 mol mol⁻¹ in those from the red clay matrix and of 0.20–0.27 mol mol⁻¹ in those from the yellow clay matrix. J.P. Muller (unpubl.) stressed that each section in such a deep profile has its own environment with regard to hydrology, pH, proximity to Al sources, organic matter content etc. during goethite formation and he suggested that the degree of substitution probably reflects these differences.

It is also possible that once formed, goethite can redissolve if reducing conditions are experienced in a modified hydrology and the newly formed secondary goethite may then display a different level of substitution. This series of successions has been interpreted as resulting from climatic changes, e.g. a transition from a dry to a wet environment. High Al substitution ($\text{Al}/(\text{Al} + \text{Fe}) = 0.20\text{--}0.25$ mol mol⁻¹) of goethite in the upper part of a bauxite profile in Surinam as against 0.09–0.13 mol mol⁻¹ in its lower part was also attributed to the formation of secondary goethite by weathering in the upper part of this profile (Grubbe et al. 1981).

Synthesis experiments indicate that the most important factor which determines the level of Al-substitution is the Al activity in solution with which structural Al is linearly correlated (see Chap. 3, Fig. 3.5 a, b). In soils, the Al activity (a_{Al}) is governed by the Al compounds, mainly Al silicates (clay minerals) and gibbsite, $\text{Al}(\text{OH})_3$, and generally increases as a_{Si} and pH go down. Accordingly, one finds high substitution in goethites from highly desilicified, gibbsitic soils, medium to high substitution in those formed in a kaolinitic matrix and low substitution in those from quartz-rich rocks, from ultramafic rocks, from the oxidation of siderite and from dissolved Fe^{2+} in lakes, i.e. all environments fairly low in a_{Al} . The effect of pH and temperature observed in synthesis experiments has not been substantiated in soils. Approximate substitution ranges for goethites in different pedoenvironments are summarized in Table 16.4.

Like their synthetic counterparts, Al-goethites from soils also show an increase in their dehydroxylation temperature with increasing Al (Schwertmann & Latham, 1986; Anand & Gilkes, 1987; Singh & Gilkes, 1992; Prasetyo & Gilkes, 1994) and a lowering of their Néel temperature and magnetic hyperfine fields at 80 and 16 K (Amarasiriwardena et al., 1988). The variation of the magnetic hyperfine field of hematites at RT (48.8–50.0 T) in Brazilian Oxisols is also, at least partly, due to Al substitution (Fontes et al., 1991).

Tab. 16.4 Approximate ranges of Al substitution in goethites of various pedoenvironments and soils

<i>Pedoenvironment</i>	<i>Soils etc.</i>	<i>Approximate range of substitution Al/(Fe + Al) mol mol⁻¹</i>
Cool, humid, redoximorphic	Gleys, Pseudogleys Massive ferricretes, Bog iron ores Lake ores	<0.1
As before but non-redoximorphic moderately acid	Alfisols, Inceptisols	0.07–0.15
Warm, humid Low Si activity Presence of gibbsite	Bauxites, Saprolites, Oxisols, Ultisols (lateritic soils)	0.15–0.35
As before but low-Al rocks	Oxisols	<0.1

16.6

Significance for soil properties

Iron oxides influence soil properties even at concentrations of only a few tens g kg⁻¹ or less, which is the case for the majority of soils. This influence is due to the functional groups at their surfaces (see Chap. 10); the number per unit weight is high due to the small crystal size and correspondingly high specific surface area. Soil properties influenced by Fe oxides are colour, association with other soil particles leading to aggregation, retention of various anions and cations at the particle surface, and electron and proton buffering. The principles of these interactions are dealt with in Chapters 6, 10 and 11, respectively. Only results obtained from soils will be discussed here.

16.6.1

Colour

Except for the top soil where the colour caused by Fe oxides is often masked by humics, most of the soil profile receives its brown, yellow or red colour from Fe oxides (Bigham & Ciolkosz, 1993). Because this is so obvious to the naked eye, soils have been named according to colour in most national classification systems, e.g. red-yellow podzols (USA), sol ochreux (France), Braunerde (Germany), krasnozem (Russia), terra rossa (Italy), and even the current modern international systems (U.S. Soil Taxonomy system and World Reference Base for Soil Resources, WRB) use colour connotations such as Rhodic (red) and Xanthic (yellow).

This reflects the fact that the colour is one of the easiest ways of distinguishing soils. Even in 1937 Alexander et al. noticed that “very red soils owe their colour to the presence of hematite”. An objective notation of soil colour is needed to describe

soils. For this purpose, the Munsell Colour System was established and special Soil Colour Charts centering in the red-yellow range are widely used (see Chap. 7). The components of the Munsell system viz. hue (shade), chroma (intensity) and value (lightness) can to a certain extent, be associated with the Fe oxide minerals and their concentration in soils (Schwertmann, 1993; Scheinost & Schwertmann, 1999). In 240 soils containing finely dispersed hematite and goethite the hue moved from 7.5 YR to 10 R as the hematite/goethite ratio increased from 0 to 1 (Fig. 16.11), whereas hues of soils containing only goethite ranged between 7.5 YR and 2.5 Y. Soils with lepidocrocite and ferrihydrite covered the in-between-range of 5 YR–7.5 YR with values >6 for lepidocrocite and <6 for ferrihydrite. These ranges are caused mainly by a variation in crystal size. Upon cementation into dense, hard masses all these colours darken (lower value) and reliable identification requires grinding.

The so-called redness rating $RR = (10-H)C/V$ originally proposed by Hurst (1977) and modified by Torrent et al. (1983) for soils. (V, C, H = Munsell value, chroma, and figure preceding YR, respectively; see chap. 6 & 7) has been used to estimate hematite concentration in soils (Torrent et al., 1980; 1983; Kemp, 1985; Torrent & Cabedo, 1986; Boero & Schwertmann, 1987) and an almost linear correlation was reported: $[\text{Hematite (g kg}^{-1})] = 0.81 + 8.4 \cdot RR - 0.75 \cdot RR^2$; $r^2 = 0.85$; $n = 21$] (Schwertmann et al., 1982a). Colour parameters of this kind, based on redness, have also been useful for general soil reconnaissance purposes in the field, especially in tropical regions where the ratio between hematite and goethite, which determines the redness, varies in some systematic and, therefore, meaningful way (Gobin et al. 2000).

The CIE systems and diffuse reflectance spectra (DRS) (see Chap. 7) have also been used for soils. By applying the CIE-Yxy system to 309 soils with varying Fe oxide

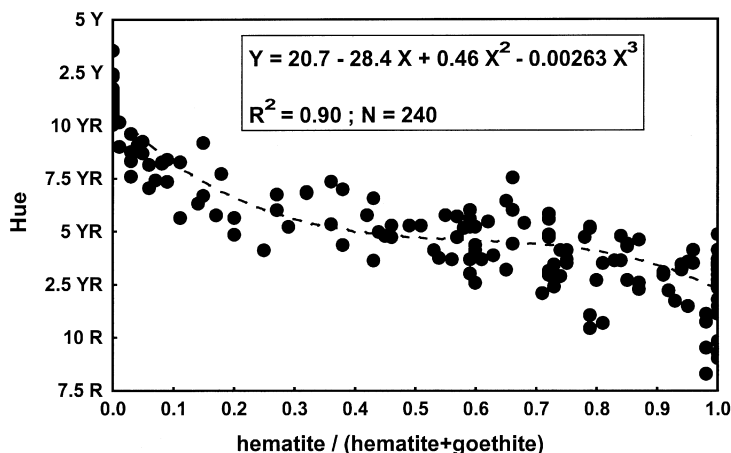


Fig. 16.11 Relationship between the the Munsell hue and the hematite/(hematite+goethite) ratio in 240 soils. Redness increases from 2.5 Y to 7.5 R (Scheinost & Schwertmann, 1999; with permission).

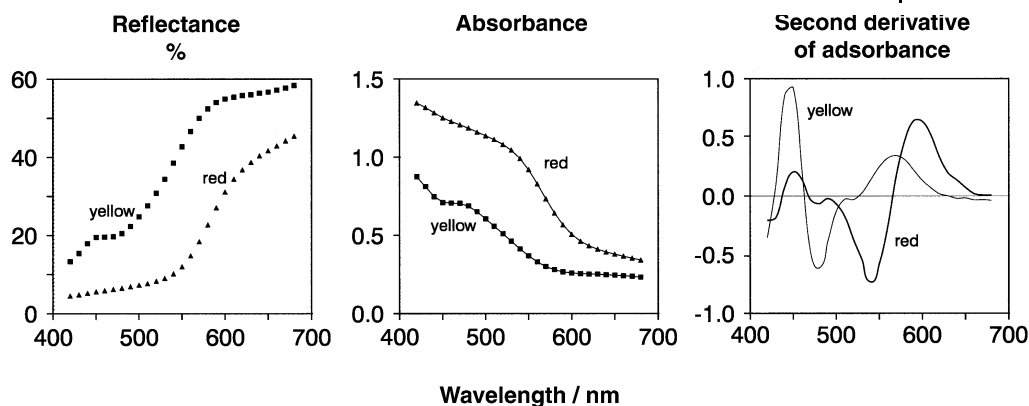


Fig. 16.12 Visible spectral reflectance (left), absorbance (middle) and 2nd derivative of absorbance (right) curves of two ground soil samples from a red B horizon of a Haplustox and a yellow B horizon of a Palexeralf (Torrent & Barrón, 1993, modified; with permission; courtesy J. Torrent).

mineralogy, those soils containing either only goethite, or hematite + goethite or lepidocrocite + goethite could be correctly differentiated to 90; 82 and 89%, respectively, whereas those containing ferrihydrite and schwertmannite could not (Scheinost & Schwertmann, 1999). Typical visible (400–700 nm) diffuse reflectance and absorption curves of a bright red (2.7YR 4.6/8.2) and a yellow (10.3 YR 7.0/5.8) soil are shown in Figure 16.12. Kosmas et al. (1984) used the 2nd derivative of DRS curves to distinguish between goethite and hematite in Brazilian Oxisols and estimated the proportion of goethite from a maximum at 447 nm and a minimum at 423 nm which were not present with hematite. Different amplitudes have, however, been found for a synthetic and a soil goethite. Maxima of the 2nd derivative were also used for the identification of various Fe oxides in kaolinitic saprolites and kaolins (Malengreau et al., 1994). For 56 goethites in a soilscape in Bavaria, a close correlation was found between b^* (yellowness) of the CIE $L^*a^*b^*$ system and their Fe oxide content ($Fe_d - Fe_o = 0.0012 b^{*2.82}$; $r^2 = 0.93$) (Scheinost & Schwertmann, 1995). The effect of moisture content on the colour values of soils is significant—the dominant wave length increased with increasing moisture content (Bedidi et al., 1992), – and this must be taken into account when different soils are compared.

16.6.2

Charge and redox properties

It is generally accepted that Fe oxides contribute to the pH dependent or variable charge of soils by ad-/desorption of *protons* (see chap. 10). The extent of this contribution is a function of the concentration and surface area rather than the type of oxide present. The assumption here is that all oxide surfaces are hydroxylated in an aqueous system. Besides the variable charge, soils also contain minerals, the clay sili-

cates, which carry negative permanent, i.e. pH-independent charge due to cation substitution.

The absolute and relative contribution of Fe oxides to the surface charge is particularly important in the highly weathered Oxisols in the tropics where Fe oxides form a significant part of the fine particle size fraction. Their influence can be recognized by a relatively high point of zero charge (pzc) (usually >5) (El-Swaify & Sayegh, 1975). An example is the soil shown in Figure 16.13 which has a pzc of ~ 6 . Although such soils often also contain gibbsite, which has a charging behavior similar to that of the Fe oxides, the high pzc is due to Fe oxides because the selective removal of the latter significantly lowers the pzc which is then dominated by the negatively charged clay minerals (Zhang & Zhang, 1992). Conversely, the addition of Fe oxides to soil minerals or soils leads to an increase in the pzc (Hendershot & Lavkulich, 1983).

In soils, *electrons* are produced by the metabolic activity of soil biota. These electrons are usually accepted by O_2 dissolved in the soil solution which is then replaced by O_2 from the soil air. Oxygen may, however, become deficient if all pores are filled with water as in waterlogged or compacted soils. Fe^{III} in Fe oxides may then function as an alternative electron acceptor and Fe^{2+} ions will be formed according to eq. (16.3). The electrons are transferred from the decomposing biomass to the Fe oxide by microbially produced enzymes. Other potential electron acceptors in soils are nitrate, Mn^{IV} and sulphate.

Active zones of Fe oxide reduction in soils can be easily recognized as bleached areas showing the grey colour of the matrix minerals after removal of the staining Fe oxides. Such zones can only form where a microbially metabolizable biomass is available, for example in the lower top soil or along roots. In poorly aerated soils with large structural units (e.g. prisms), root mats often develop only at the surface of these units and bleach their surfaces, whereas the interior is still coloured

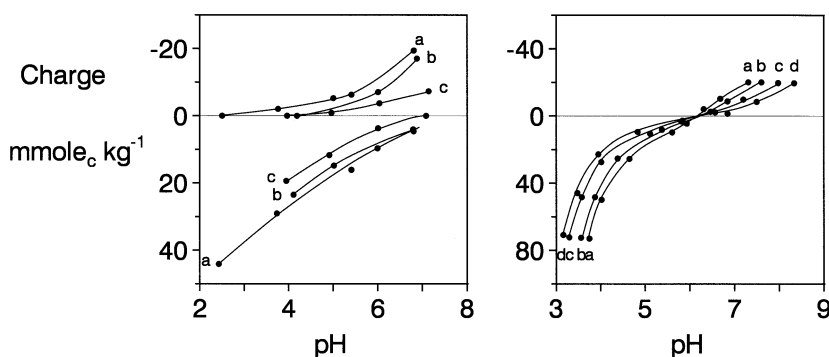


Fig. 16.13 Charge properties as a function of pH of an oxidic-kaolinitic Oxisol B horizon (Brazil) with ca. $300\ g\ kg^{-1}$ Fe oxides as determined (left) by Na and Cl adsorption from a) 0.2;

b) 0.1 and c) 0.01 M NaCl solution and (right) by potentiometric titration in a) 1; b) 0.1; c) 0.01 and d) 0.001 M NaCl solution

(Van Raij & Peech, 1972; with permission).

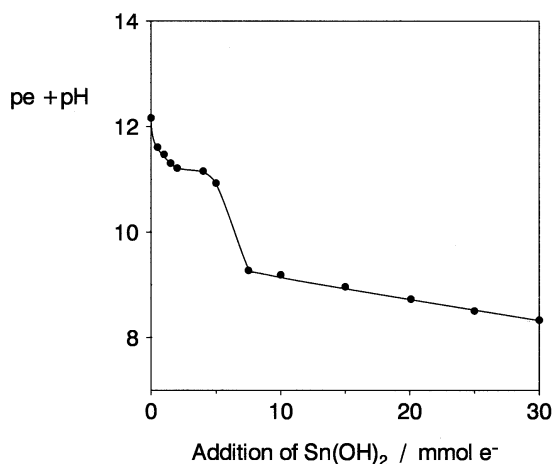


Fig. 16.14 Electron titration curve of a soil with Sn(OH)_2 as a reductant. Equilibration time 14 days (Lindsay & Sadiq, 1983; with permission).

(Schwertmann, 1993). Such soils are characterized by a hydraulic conductivity somewhere in the profile which is too low to cope with the high rainfall, so that all pores will be filled with water for certain periods of time (see above). In this case, the oxygen supply is limited by the low level of O_2 dissolved in the soil water ($46 \text{ mg O}_2 \text{ L}^{-1}$ at 25°C) and reduction of Mn-oxides, nitrate and Fe oxides sets in. Soils containing Fe oxides are, therefore, redox-buffered (poised). The redox titration curve (Fig. 16.14) of a soil with 23 g kg^{-1} Fe as Fe oxides shows buffering at two different pe + pH levels, one at ca. 11 and another at ca. 9, which indicate the presence of a more reducible (e.g. ferrihydrite) and a less reducible (e.g. goethite) Fe oxide, respectively, in accordance with their different solubilities (see Chap. 9).

16.6.3

Anion and cation binding

The binding of cations and anions by Fe oxides through surface adsorption (see Chap. 11) and/or incorporation (see Chap. 3) makes soils important sinks for a range of compounds such as heavy metals, phosphate and sulphate. This can be derived from significant correlations between such compounds and the Fe oxide content of the soils.

Of the anions, *phosphate*, as an essential major plant nutrient has attracted specific attention due to its high affinity for Fe oxides. Phosphate sorption was found to be positively correlated with Fe_d (Borggaard, 1983a; Peña & Torrent, 1984; 1990; Singh & Gilkes, 1991) and increased with increasing contact time (Fig. 16.15). The oxalate soluble Fe oxides (Fe_o) appear more efficient than the rest, possibly because of the higher surface area of the ferrihydrite which is extracted by oxalate (Borggaard et al., 1990). In most of these soil experiments the Fe oxide minerals have not been identified. In 46 goethitic-hematitic soils from Spain no difference in P retention by the two oxides could be observed (Peña & Torrent, 1984; Torrent, 1987). In an Oxisol topequense from Brazil (see Fig. 16.2), the P adsorption maxima increased from the

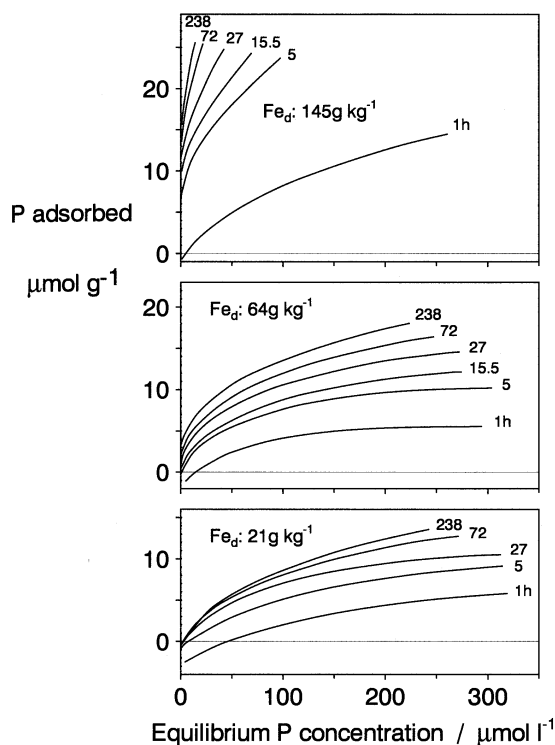


Fig. 16.15 Phosphate adsorption curves of three low moor soils with different goethite content as a function of contact time (1–238 h) (Schwertmann & Schieck, 1980; with permission).

hematitic upper slope soils to the goethitic soils in the depression and this was attributed to the smaller crystal size of goethite (MCL_{111} : 16–26 nm) compared to that of hematite (MCL_{110} : 29–44 nm) (Curi & Franzmeier, 1984). In line with this result, P adsorption and desorption data for 11 Brazilian Oxisols (Fontes and Weed, 1996) and 12 *Terre rosse* (Red Mediterranean soils on limestone), showed a significant relationship with their goethite but not with their hematite contents (Colombo et al., 1991). Residual phosphate in the low-humic subsoils of highly weathered soils may even be occluded in Fe oxide accumulations, since it is only released upon dissolution (Smeck, 1985; Walker & Syers, 1976; Smeck et al., 1994). Penetration of fertilizer P into porous, ferruginous nodules thereby removing 180 kg P ha^{-1} from plant-available pools in three years was observed in such soils (Ghana; Brazil). This shows that such nodules are by no means inert (Tiessen et al. 1991). The nodules contained between 430 and 900 mg P kg^{-1} as against 80 – 280 mg P kg^{-1} in the soil fines (Abekoe & Tiessen, 1998).

Synthetic goethites with various crystal morphologies adsorbed $2.51 \pm 0.17 \mu\text{mol P m}^{-2}$ in agreement with the surface site density of two, contiguous, singly coordinated FeOH groups (see Chap. 10 & 11). A similar value of $2.62 \pm 0.52 \mu\text{mol m}^{-2}$ was found for 10 goethite-rich natural samples from soils and similar material (Torrent et al., 1992) and for soils from Denmark and Tanzania (Borggaard, 1983a). These observations are in line with TEM observations which showed that crystals of

natural goethite are, like synthetic ones, bounded predominantly by (101) faces (see Fig. 4.4 & 4.5). The situation for soil hematites is not so clear. It was postulated earlier that only the prismatic faces of the crystals (mainly 110) carry singly coordinated FeOH groups and are, therefore, active in anion adsorption. The density of these groups at the (101) face should result in ca $4.2 \mu\text{mol m}^{-2}$ of P adsorption at full coverage. A value of $4.05 \mu\text{mol P m}^{-2}$ was obtained when the negative relation between the amount of P adsorbed and the crystals width-to-thickness ratio ($\text{MCL}_a/\text{MCL}_c$) was extrapolated to $\text{MCL}_a/\text{MCL}_c = 0$, i.e. to crystals of infinite length along c (= only prismatic surfaces) (Fig. 16.16).

Because of the high affinity of Fe oxides towards phosphate, waste material rich in Fe rich oxides has been added to soils to improve their P-adsorption capacity. A well-known example is the so-called *Red Mud*, an Fe oxide-rich waste product of the aluminum industry in which the Fe oxides of the bauxite ore are concentrated after leaching the Al. Pasture growth on acid, sandy soils in Western Australia could be increased and leaching of phosphate could be reduced, by adding moderate amounts of red mud ($10\text{--}20 \text{ t ha}^{-1}$). At these rates, no ground water contamination was observed and no gypsum was required to counteract the high pH of the mud due to caustic soda (Summers et al. 1996). In calcareous soils, phosphate from fertilizer is not available due to transformation into sparingly soluble Ca-phosphates, but this transformation can be effectively retarded by adding ferrihydrite which competes with the phosphate and keeps it accessible to plants (Rahmatullah and Torrent, 2000). The phyto-availability of P adsorbed on Fe oxides to sunflowers was lower for goethite than for hematite and 2-line ferrihydrite (Guzman et al. 1994).

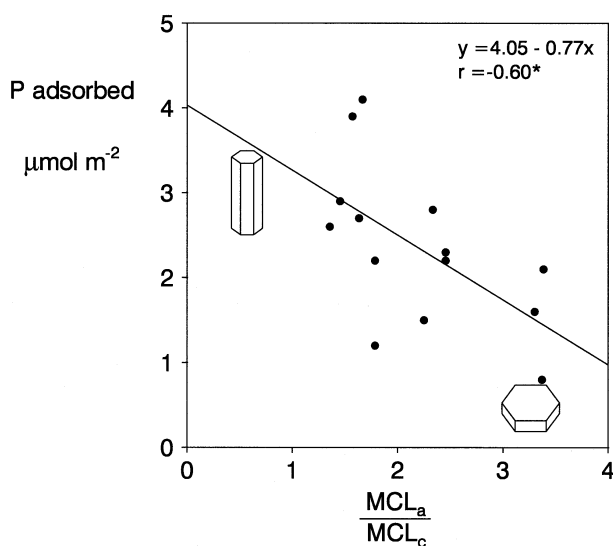


Fig. 16.16 Adsorbed phosphate of natural hematitic material as a function of the aspect ratio width/thickness (Torrent et al., 1994; with permission).

Phosphate must be applied as fertilizer to the soil. Ideally it is added in quantities sufficient to guarantee optimal yields, but not in excess in order to avoid P transportation into other compartments of the ecosystem. The amount added should be based on an accurate estimation of the plant-available fraction of P already present in a soil. This is an old and difficult task and a large number of extraction methods have been used since intensive land use was practised. Recently methods have been worked out in which a strip of filter paper impregnated with an Fe oxide (2-line ferrihydrite) is dipped into a soil suspension and the amount of P adsorbed by the paper is taken as being plant-available (Sissingh, 1988; Van der Zee et al., 1987; Sharpley, 1993; Sharpley et al., 1994; Kuo and Jellum, 1994; Myers et al. 1997). Anion and cation resins extracted more P from four heavily fertilized soils than from goethite (Delgado & Torrent, 2000). Other oxyanions adsorbed by soil Fe oxides are silicate, arsenate, chromate, selenite (?) and sulphate. Adsorption of sulphate led to a release of OH^- ions and was substantially lowered once the Fe oxides were selectively removed (Fig. 16.17).

In connection with the carbon storage in the pedosphere, an interest in the extent and mechanism of the retention and stabilization of *humics* by Fe oxides has arisen. A number of soil studies showed significant correlations between the total or fractional content of carbon and Fe (see review by Kaiser & Guggenberger, 2000). For example, positive correlations were found for a range of soils between the total or pyrophosphate-extractable carbon and oxalate-extractable Fe + Al (Turchenek & Oades, 1979; Adams & Kassim, 1984; Evans & Wilson, 1985; Shang & Tiessen, 1998). It has to be kept in mind, however, that the oxalate also extracts organically bound Fe and Al. Removal of Fe oxides from a soil also reduced the adsorption of dissolved soil organic matter (DOM) (Kaiser & Zech, 2000). These results have led to a number of studies on the adsorption of DOM by synthetic Fe oxides (see chap. 11). From the mixture of organic compounds in DOM, Fe oxides preferentially adsorbed aromatic as against aliphatic, hydrophobic as against hydrophilic and high molecular as

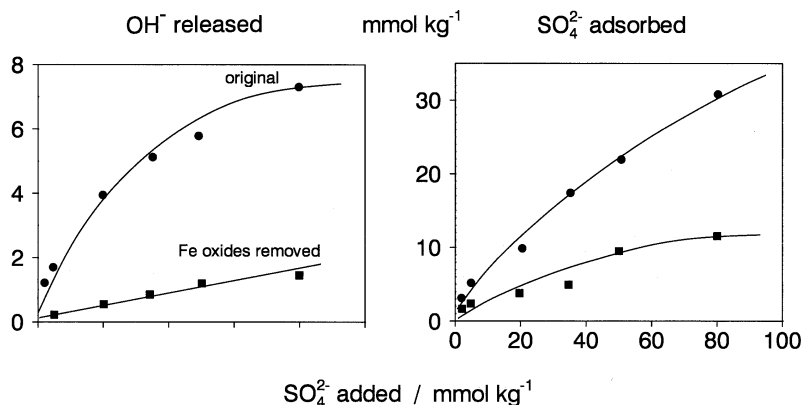


Fig. 16.17 Sulphate adsorption and OH^- release curves of an Oxisol (Brazil; Fe_d : 77 g kg^{-1}) before and after removal of Fe oxides (Zhang et al., 1991; with permission).

Tab. 16.5 Correlation coefficients with Fe and accumulation factors with respect to parent rock concentrations of various trace elements in laterites (Data from 1) Schellmann 1986 and from 2) Singh & Gilkes, 1992).

<i>Element</i>	<i>Laterites from basalts¹⁾</i> <i>(n = 51)</i>	<i>Lateritic soils of Western Australia²⁾</i> <i>(n = 39)</i>	
	<i>Accumulation factor with respect to parent rock</i>	<i>Range of concentration*</i>	<i>Correlation coefficient with Fe concentration</i>
Fe	1.9	12–154	–
Al	1.8	14–144	0.27
Ti	1.9	0.3–22	0.56
Cd	–	0.5–4.3	0.81
Co	0.93	13–368	0.71
Cr	2.1	10–298	0.51
Cu	1.4	0.6–188	0.78
Mn	0.75	14–1382	0.57
Ni	1.4	11–160	0.61
V	2.1	33–651	0.92
Zn	1.1	2–83	0.69

* mg kg^{-1} ; except Fe, Al, Ti in g g^{-1}

against low molecular weight moieties (Chorover & Amistadi, 2001). Similarly, B horizon material of two Inceptisols containing ca. 30 g kg^{-1} Fe_d preferentially adsorbed aromatic and carboxyl C from DOM of a Podzol O horizon as against alkyl-carbon (Kaiser et al., 1997). Stable humic-goethite associations have been observed in an Oxisol from Brazil (Fontes et al., 1992). A 0.1M NaOH extract contained up to 22% carbon and up to 50% high-Al goethite which consisted of isodimensional particles, 8–12 nm across. The adsorbed humic acid imparts a high negative charge to the goethite surface and leads to its effective dispersion at high pH.

Table 16.5 shows that during soil formation many *heavy metals* are concentrated in the soil relative to the parent rock to a similar extent as is Fe (left part of the table) and are, therefore, correlated with the Fe content of the soils (right part). Iron-manganese nodules may, therefore, have higher concentrations of certain elements than the surrounding soil material. An adsorption experiment with Pb on a soil ferrihydrite showed the same pH dependency as with a model sorbent but a ca. 100 fold higher Pb activity in solution at a Pb load of 20 mg kg^{-1} , probably due to competitors (Si, humics) being adsorbed by the soil ferrihydrite (Sauve et al. 2000). Therefore, when soil Fe oxides are extracted, a large fraction of trace metals is often also released (Fig. 16.18) (Zeien and Brümmer, 1991; Singh & Gilkes, 1992; Trolard et al., 1995; Palumbo et al., 2001). The adsorption of Co at pH < 6 by an Oxisol containing ca. 100 g kg^{-1} Fe, mainly as goethite, fell drastically after removal of the Fe oxides by dithionite (Bibak et al., 1995). In a rice-growing (paddy-) soil, selective removal of Fe oxides increased the fixation of NH_4^+ by three-layer silicates. This may depress the nitrogen supply to paddy rice because Fe oxides are usually reductively dissolved during the wet, anaerobic period of these soils (Scherer and Zhang, 1999).

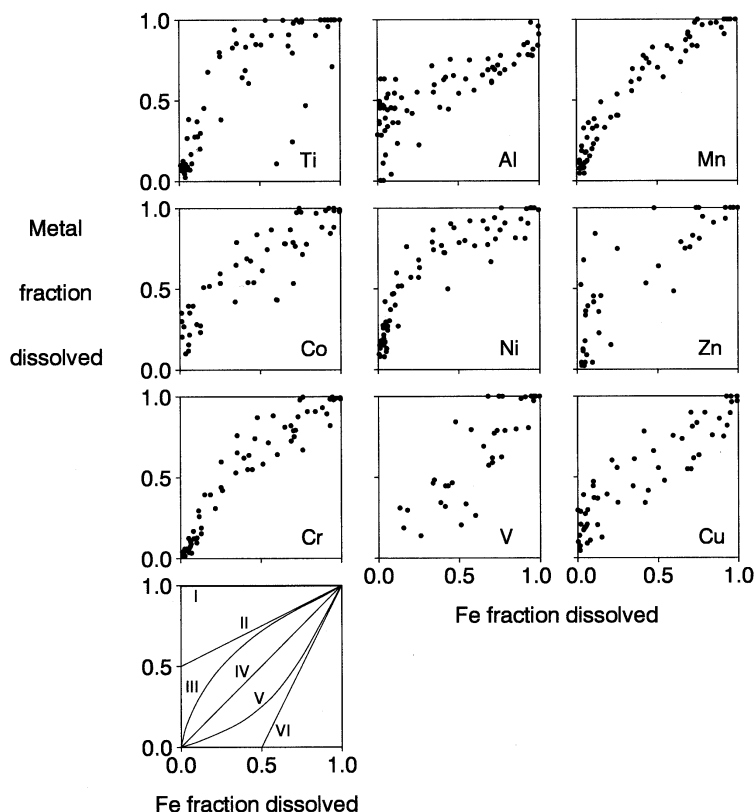


Fig. 16.18 Relationship between dissolved fraction of various metals and dissolved fraction of Fe (1M HCl; 40 °C) in Fe oxide concentrates of West Australian soils. The lower left graph shows the plots that could be obtained for different distribution of the metal in the Fe oxide: curve I: location of the metal at the Fe oxide surface; curve VI: location in the centre; curve IV: perfect congruency; curves II, III and V: intermediate situations (Singh & Gilkes, 1992; with permission).

As in pure systems, the adsorption of anions and cations on iron oxides is strongly pH dependent. This has to be kept in mind when an optimum pH is to be obtained with liming. The adsorption of phosphate, arsenate etc. increases as the pH falls below 7, whereas the adsorption of heavy metal cations rises as pH goes up (see eq. 11.18 & 11.19). Therefore, as soils become more acidic, heavy metals will be released into the soil solution. Conversely, liming soils has the opposite effect.

16.6.4

Aggregation and cementation

In addition to chemical and mineralogical alterations, weathering and soil formation also induce physical changes in the rock. A more or less dense, non-porous, massive rock turns into a porous material containing air and water and thereby becomes suit-

able for root development and growth of plants and soil biota. Among the numerous processes leading to such physical alterations are those of aggregation and cementation. In both cases, primary particles are associated to form larger units in which the internal cohesive forces are substantially higher than those between the units. Aggregation is mainly based on surface charge and electric double layer properties, hence aggregation is reversible and sensitive to pH and electrolyte type and concentration. In contrast, in cementation which is usually much more stable than aggregation, solid-solid contact through chemical bonding may be involved; this is not responsive to classical dispersion treatments and requires destruction of the cement. It is accepted that there is no clear separation between the two mechanisms and combinations will certainly exist.

Iron oxide participation in aggregation and cementation is well known. Examples in which aggregation is involved are tropical soils (Ultisols and Oxisols) in which most of the clay particles $< 2 \mu\text{m}$, consisting predominantly of kaolinite, are aggregated into secondary particles about $5\text{--}300 \mu\text{m}$ in size; these are extremely stable under mechanical stress and make these clay soils highly permeable to water. The iron oxide content of these aggregates ranges between 50 and 200 g kg^{-1} and consists of mixtures of goethite and hematite.

Microscope observations and chemical analyses help locate the Fe oxides in the fabric of matrix soil particles. Single Fe oxide-containing aggregates which appear uniform to the naked eye, may vary appreciably in Fe content and mineralogy (Fordham & Norrish, 1979). SEM and TEM photos show goethite and hematite crystals in strongly developed soils to be associated in a more or less systematic fashion with flakes of kaolinite, usually the main matrix mineral in such soils (Fig. 16.19 a–c) (see also Kitagawa, 1983). In stacks of kaolinite flakes, so-called books, goethite may partly fill the interflake space (Fig. 16.22 c, Muller, 1987). On the other hand, “clean” kaolinite crystals together with small aggregates consisting almost solely of Fe oxides, have also been found (Fig. 16.19 d) (Greenland et al., 1968; Jones et al., 1982; Schwertmann & Kämpf, 1984; Torrez Sanches et al., 1990). An association of small hematite crystals on large tabular gibbsite crystals was found in bauxitic saprolites from Nigeria (Fig. 16.19 e).

Selective removal of the Fe oxides usually, but not always (Kretzschmar et al., 1993), leads to destruction of the aggregates. Other chemicals which removed only little Fe have also led to substantial dispersion of such aggregates (Cambier & Picot, 1988; Pinheiro-Dick & Schwertmann, 1996). As seen in Table 16.5, this was the case for citrate which was almost as effective as dithionite. The mechanism of dispersion by citrate is not known as yet. It is likely that the organic ligand is adsorbed on the Fe oxide surface which becomes more negative so that the bond to the negatively charged kaolinite surface is dissolved. It is also possible, however, that a chemical Si-O-Fe linkage between kaolinite and Fe oxide breaks down. Addition of phosphate to two Fe-oxide-rich Oxisols (goethite $>$ hematite) modified their dispersion behavior by changing the size and sign of the surface charge of the Fe oxides: low additions lowered the positive charge and the extent of dispersion, whereas with higher P additions, the net charge was reversed and dispersion increased (Lima et al., 2000).

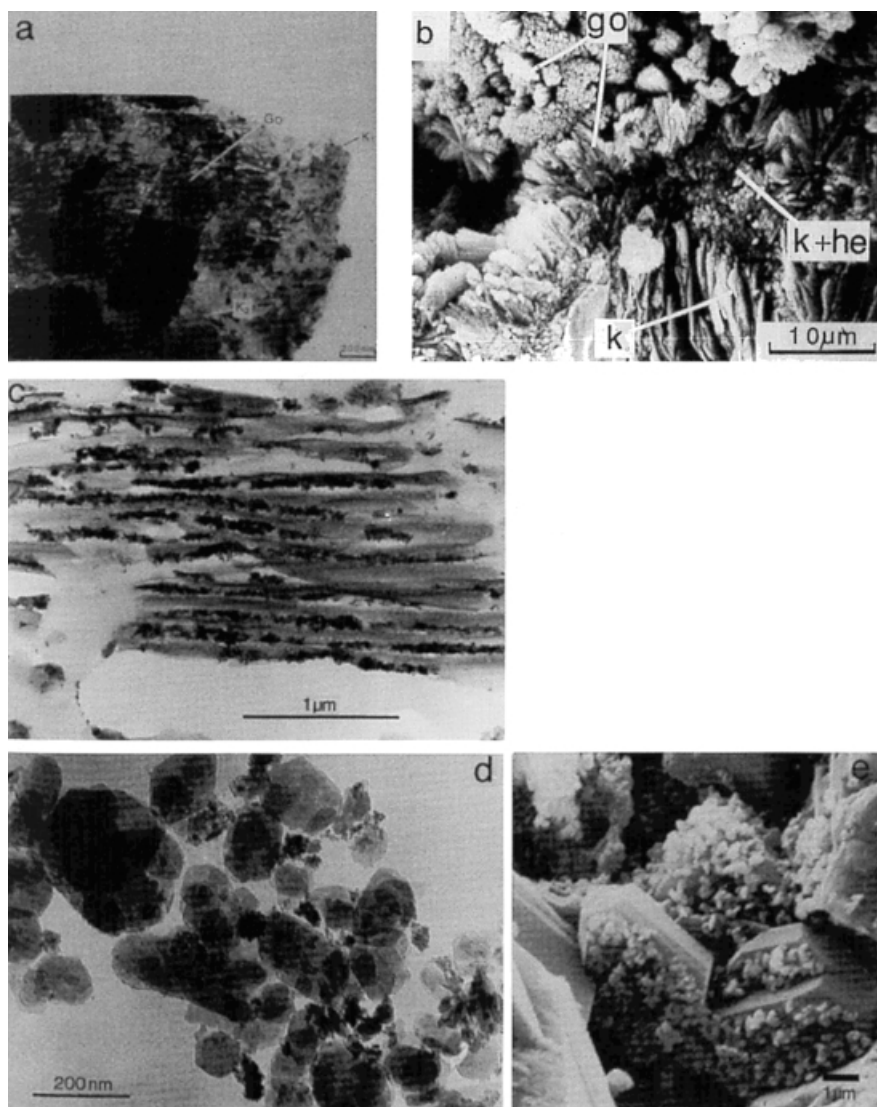


Fig. 16.19 Electron micrographs of natural associations between iron oxides and other soil minerals. a) Goethite (Go) crystals epitaxially grown on kaolinite (K) flakes (TEM) from a laterite in Cameroon (courtesy J.P. Muller; see also Boudeulle & Muller, 1988). b) Association of kaolinite (k), goethite (go) and hematite (he) in an Oxisol, Cameroon (SEM) (1987; courtesy J.P. Muller; see Muller & Bocquier, 1986). c) Goethite accumulation between kaolinite

flakes (TEM of thin section) (see Tandy et al., 1988; courtesy D. Tessier). d) Clay fraction of an Oxisol Ap horizon from Puerto Rico with kaolinite platelets and goethite aggregates; bar = 50 nm (courtesy R.C. Jones); Jones et al., 1982; with permission) e) Small hematite crystals associated with large, tabular gibbsite from a bauxitic saprolite on basalt (SEM), Jos Plateau, Nigeria (see Zeese et al., 1994; courtesy G.F. Tietz).

Tab. 16.6 Yield of clay particles $< 2 \mu\text{m}$ from 100–200 μm aggregates (Fe_d : 106 g kg^{-1}) of a Brazilian Oxisol after various dispersion treatments (Data from Pinheiro-Dick & Schwertmann, 1996)

<i>Treatment</i>	<i>Fe extracted</i> <i>g kg⁻¹</i>	<i>Clay</i> <i>g g⁻¹</i>	<i>Dispersion</i> <i>(DCB = 1)</i>
Dithionite-citrate-bicarbonate (DCB)	106	760	1.0
H ₂ O, 2 h shaking	n.d.*	0	0
H ₂ O, 16 h shaking, pH 8.5	n.d.	60	0.08
NaH ₂ PO ₄ , 0.24 M	0.014	220	0.29
NaHCO ₃ , 0.2 M, pH 8.5	n.d.	320	0.42
NH ₄ oxalate, 0.2 M, pH 3.0	2.81	400	0.53
Na citrate-bicarbonate, pH 8.5	0.74	620	0.82
Na citrate, 0.2 M, pH 8.5	0.41	640	0.84

* n.d. = not detectable

Fe oxides are added to poorly structured soils to foster aggregation. Addition of ferrihydrite, goethite, lepidocrocite and hematite to a poorly structured loessial soil aggregated the soil with the effectiveness of aggregation increasing as the surface area of the oxide increased (Schahabi & Schwertmann, 1970). Adding 2-line ferrihydrite to the poorly structured, easily dispersable, so called hard-setting, soils of the semi-dry tropics increased aggregation and structural stability in the wet stage, whereas the tensile strength in the dry state decreased. There was a positive correlation between oxalate soluble Si and the amount of ferrihydrite added, so it was suggested that the added ferrihydrite reacted with soil silicates to form -Fe-O-Si- bonds, thereby promoting aggregation (Breuer and Schwertmann, 1999).

Model experiments were also carried out to simulate the interactions between Fe oxides and soil constituents. TEM observations (Fig. 16.20a, d) and electrophoretic measurements (Fig. 16.21) showed that in acid media, small, positively charged ferrihydrite particles interact with the negative silicate surface (Oades, 1984). The pzc of the soil clay (ca. 2) increased with the amount of Fe added, indicating that the negative charge of the kaolinite was gradually neutralized through an interaction with the positively charged ferrihydrite. At full neutralization, the electrophoretic mobility was at its minimum and the clay was fully flocculated. With higher Fe oxide contents, the charge reversed and the surface of the clay minerals had a pzc identical to that of Fe oxides (see also Chap. 10).

No interaction between ferrihydrite and kaolinite was found at pH 9 because both compounds are negatively charged at this pH (Fig. 16.20b, c). Boiling kaolinite and montmorillonite in a $\text{Fe}(\text{NO}_3)_3$ solution for 8 min resulted in clays containing up to ca. 55 mg oxalate soluble Fe/g clay. The BET surface area of kaolinite increased from 18 to 34 m^2/g and that of montmorillonite from 11 to 62 $\text{m}^2 \text{g}^{-1}$. Whereas kaolinite shows only a small decrease in $> 10 \mu\text{m}$ pores, montmorillonite lost about half of its $> 10 \mu\text{m}$ pores even with the lowest Fe oxide content (6.6 mg $\text{Fe}_o \text{ g}^{-1}$ clay). It has been speculated that in contrast to kaolinite, the Fe oxide, in the presence of montmorillonite, remained highly disorderd and active due to Al and Si dissolved from

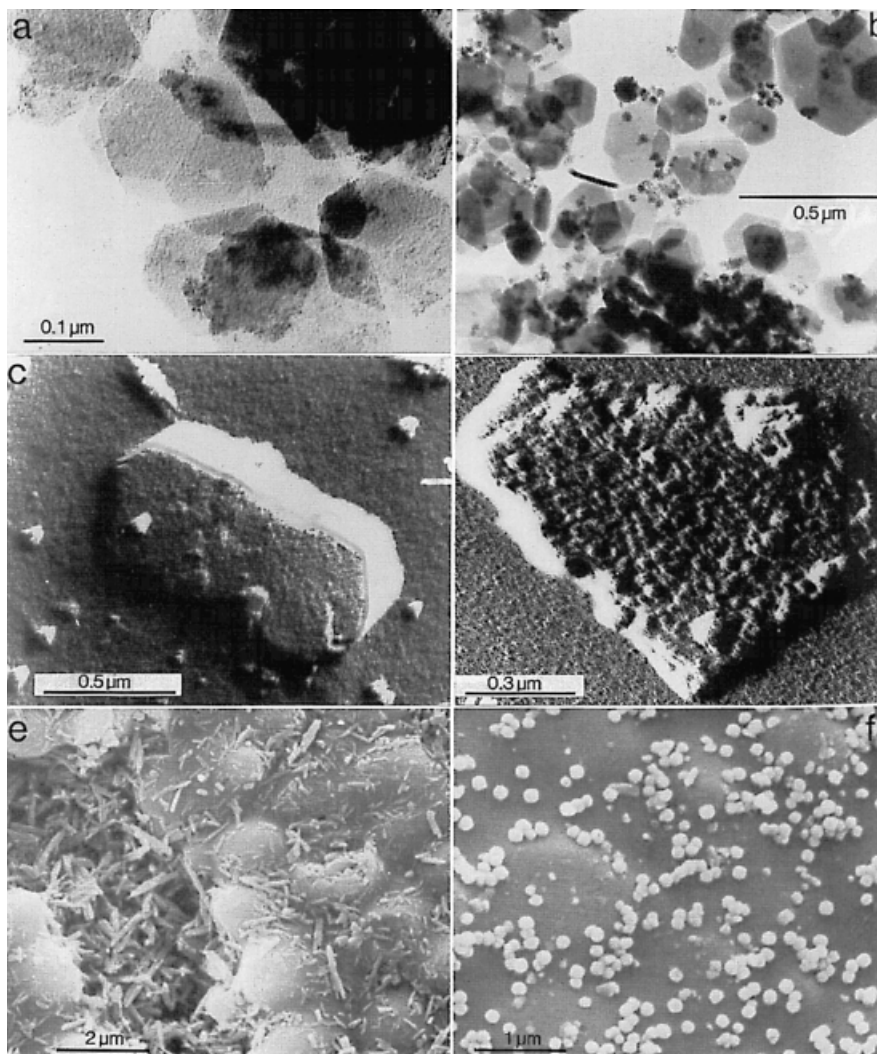


Fig. 16.20 Electron micrographs of synthetic associations between iron oxides and Si-minerals. Normal (a, b) and shadowed (c, d) kaolinite – 6-line ferrihydrite associations at pH 3 (a, d) and 9 (b, c) (Saleh & Jones, 1984; with permis-

sion; courtesy A.A. Jones). Goethite (e) and hematite (f) crystals attached to large cristobalite particles (Scheidegger et al., 1993; with permission courtesy A. Scheidegger).

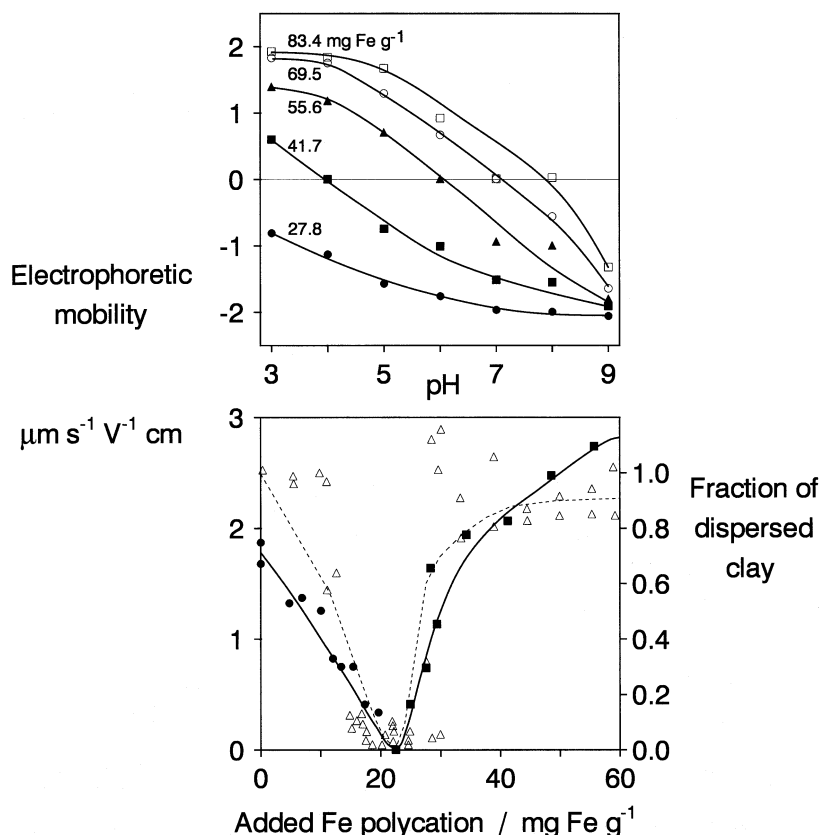


Fig. 16.21 Top: Electrophoretic mobility of a soil clay (kaolinite, illite, interstratified minerals) after addition of 27.8–83.4 mg Fe g^{-1} as hydroxy polymers of $10^4 - 5 \cdot 10^4$ nominal molecular weight, a size of ca. 5 nm, and a positive charge of $0.2 \text{ z}^+/\text{Fe}$. Bottom: Electrophoretic mobility (solid line) and fraction of dispersed clay (dashed line) as a function of the amount Fe hydroxy polymers; J negative and B positive electrophoretic mobility P (Oades, 1984; with permission).

the clay and that it is retained between the clay domains rather than between the unit layers (Celis et al., 1998).

A widely used method for producing physically stable Fe oxide bodies for percolation experiments, suggested by Scheidegger et al. (1993), is to simply shake quartz or cristobalite sand with an Fe oxide suspension (Fig. 16.20e, f). At a pH of 7.9, cristobalite adsorbed up to ca. 40 mg m^{-2} of goethite ($\text{SA: } 21.3 \text{ m}^2 \text{ g}^{-1}$). The adsorption was explained by the neutralization of the negative charge at the SiO_2 surface by the positive charge of goethite. Adsorption followed the Freundlich isotherm ($y = 1.13 x^{0.254}$; y = goethite adsorbed (g L^{-1}), pH 2.5, $I = 0.01 \text{ M}$, 25°C). Neither $M \text{ HNO}_3$ nor 10 M NaOH was able to desorb the goethite. On the basis of XPS it is postulated that stable Si-O-Fe bonds were formed and it can be speculated that bonds of

this nature also form in soils. Support for the involvement of Si in this interaction in soils comes from significant relationships between the degree of aggregation and the ratio of oxalate-soluble Si to Fe (Colombo & Torrent, 1991). These results suggest that besides electrostatic forces, Van der Waals forces or even chemical bonds play a role in establishing such highly stable associations.

Examples of *cementation* by Fe oxides are concretions and Fe-rich soil horizons such as ferricretes. They are widespread in regions of the old Gondwana surfaces in Africa, South America and Australia but occur also in ground water soils of young Pleistocene landscapes in temperate regions (e.g. bog iron ores). These formations contain more Fe (200–800 g Fe oxides kg⁻¹) than aggregates and are extremely hard and stable under mechanical or chemical treatment. They are, therefore, used for road construction in areas where no solid rocks are easily available as in many tropical regions. Roots normally cannot penetrate these formations. The thin section in Plate 16.II shows quartz grains cemented by palisade-like goethite layers which fill most of the intergranular pores (see also Zeese et al., 1994).

17

Organisms

17.1

General

Many living organisms, prokaryotes and eucaryotes produce inorganic solids, the so-called biominerals. The best known biominerals are the carbonates and oxalates of calcium (calcite, apatite, vaterite, whewellite and weddellite), silicon oxide and the oxides, sulphides, carbonates and phosphates of iron. The best known example of an Fe oxide is magnetite which is formed within the cells of magnetotactic bacteria. Formation of biominerals follows one of two pathways (Lowenstam, 1981): it can be *directed* (mediated) by the provision of an organic support or surface such as a membrane (organic matrix mediated or boundary organized mineralization) or *induced* by creating a suitable chemical environment (biologically controlled mineralization). In the case of mediated formation, the type and properties of the iron oxide are strongly influenced by the organism. Induced Fe oxide formation is achieved by so-called chemo- or lithotrophic organisms which gain energy from the oxidation of Fe^{2+} which in turn, leads to extracellular precipitation of the Fe^{III} oxide. It has been estimated that 90.1 mol of Fe^{2+} must be oxidized for one mol of carbon to be assimilated (Ehrlich, 1990). Although the nature of the Fe oxide formed depends essentially on the physical and chemical environment, it has been postulated that the external surface of the bacterial cell may act as a template or nucleation medium (see below). The subject of bacterial Fe mineralization is extensively discussed by Konhauser (1998) who also raised the interesting, but so far unanswered, question of whether the bacteria derive any benefit from the induced mineral precipitation at their surfaces.

With the exception of hematite, all the major iron oxides are found in living organisms. The absence of hematite suggests that biological environments do not provide suitable conditions for the formation of this oxide. Like other biominerals, biotically mediated iron oxides have various homeostatic functions, i.e. maintenance of steady states (Williams, 1991); they participate in iron metabolism, act as magnetic navigational devices and can provide support, hardness and density in structures such as teeth. Owing to their extremely low solubility, they serve as sinks for toxic Fe^{2+} ions. An overview of those iron oxide biominerals known to date and the organisms in which they are found, together with their functions, is given in Table 17.1. There is no doubt that in the future, iron oxides will be discovered in an increasing number of different organisms.

Tab. 17.1 Iron oxide minerals in biota and their functions

Organisms	Functions	Main Fe oxides
Bacteria	Metabolic byproduct	Ferrihydrite
	Magnetotaxis	Magnetite
Limpets	Teeth hardening	Goethite
Chitons	Teeth hardening	Magnetite (lepidocrocite, ferrihydrite)
Salmon, honey bees, pigeons	Navigation	Magnetite
Plants	Fe storage	Ferrihydrite (in phytoferritin)
Many organisms including man	Fe storage	Ferrihydrite (in ferritin)

Adapted from Frankel (1991) and Mann et al. (1989 a) with permission

The field of biomineralization has experienced a marked upsurge in interest in recent years. Reviews of progress include those of Westbroek and de Jong (1983), Kirschvink et al. (1985), Mann et al. (1989 a), Lowenstam and Weiner (1989), Frankel and Blakemore (1991), Skinner and Fitzpatrick (1992), Banfield and Nealson, (1997), Bäuerlein, (2000) and Mann (2001). Much of the research has concentrated on biological details and the properties of the organic matrix in which the oxides are deposited. Studies of the actual biominerals have been concerned with their identification and characterization. As Addadi and Weiner (1992) point out, however, the understanding of the *in vivo* mechanisms of biomineralization is still at the descriptive stage and it is in this direction that further research should be concentrated.

17.2

Biotically-mediated formation

17.2.1

Goethite and lepidocrocite

Goethite is found in the yellow-brown, radular teeth of limpets (a type of mollusc, *Patella vulgata*). Iron was first detected in these teeth as early as 1856 (Tröschel), but the mineral was only identified as goethite (by XRD) ca.100 years later (Lowenstam, 1962). The goethite-hardened teeth are distributed along a radula (a tongue-like organ) and are used for grazing on algae growing on rocks in the intertidal zone. Grazing involves scraping the rocks during which process the teeth are abraded and must be continually replaced. The radula acts like a conveyor belt and transports the teeth forward as they mature. In the mature teeth, the goethite crystals are present as rather irregular needles (like abiotic goethites) up to 1 µm in length and 20 nm wide (Fig. 17.1). They are single domain, elongated in the [010] direction and are aligned parallel to the fibres of the organic matrix in which they are embedded (Mann et al., 1986). The irregular edges of these crystals are probably the result of interactions during growth with either the organic matrix or with silicate and phosphate which are also present in the tooth. These crystals could have been formed either by direct

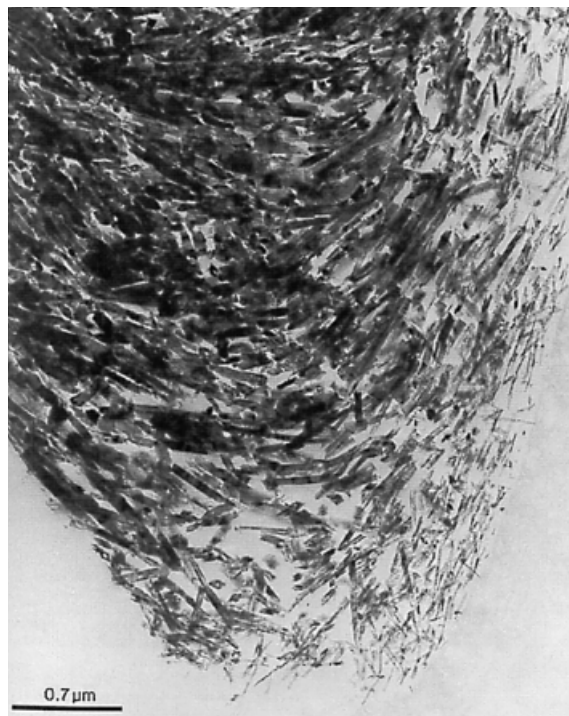


Fig. 17.1 Electron micrograph of the cusp tip of a limpet tooth showing the alignment of acicular goethite parallel to the tooth posterior edge and the changing orientation within the central region (courtesy S. Mann).

precipitation via oxidation of Fe^{II} solutions (Mann et al., 1986) or by rapid transformation of ferrihydrite, present at the base of the teeth, via reduction by interaction with an organic, sulphur containing, reducing ligand such as cysteine (Cornell & Schneider, 1989). On kinetic grounds, both mechanisms appear to be feasible; in the presence of cysteine, goethite forms at physiological pH and temperature from ferrihydrite (*in vitro*) as rapidly as it precipitates by oxidative hydrolysis of Fe^{II} ions. The amount of ferrihydrite present at the base of the teeth decreases as the teeth mature and goethite forms (Mann et al. 1986) which is consistent with the concept of ferrihydrite being a precursor of goethite in these organisms.

Biogenic *lepidocrocite* was first discovered by Lowenstam (1967) in the radula teeth of a chiton. The crystals are lath-shaped and several tenths of μm long with terminal $\{101\}$ faces (Webb et al., 1989) (see Fig. 4.14a). The lepidocrocite is often associated with magnetite and ferrihydrite suggesting an Fe^{II} precursor (see Chap. 13).

17.2.2

Ferrihydrite

Ferrihydrite is the iron oxide with the most widespread distribution in living organisms. In the form of *ferritin*, an iron storage protein, it is found in all organisms from bacteria through to man (in heart, spleen and liver). It occurs in plants as phytoferritin (review by Seckback, 1982). Ferritin plays a key role in iron metabolism; it maintains

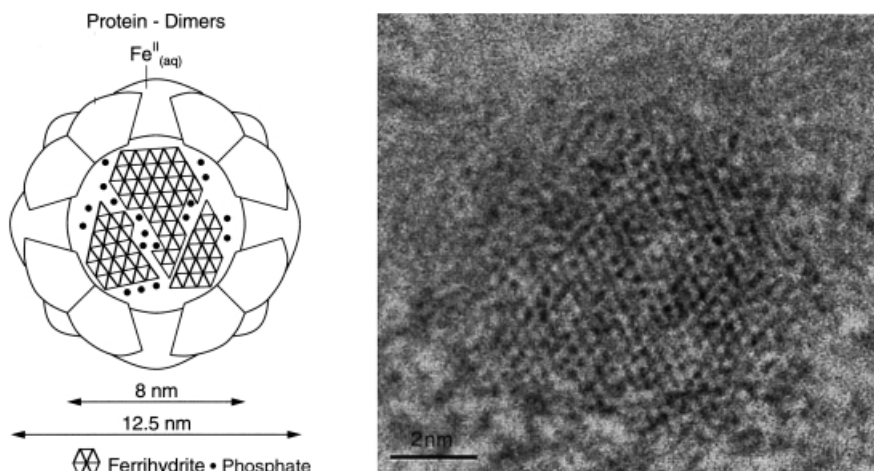


Fig. 17.2 Left: A schematic picture of ferritin. (Mann, 1986, with permission;). Right: Lattice image of a single domain of ferrihydrite from the inorganic core of a human ferritin molecule. The fringes of ca. 0.27 nm correspond to the (110) plane (bar is 2 nm) (courtesy S. Mann).

the iron required by the organism in such a state that it is stored in an inert form and yet can be readily mobilized as a soluble species when required by the tissues.

Ferritin consists of an iron core (5–10 nm across) containing 2000–3000 Fe atoms (Harrison et al., 1989) enclosed in a roughly spherical protein shell (Harrison et al., 1967; Harrison & Hoy, 1973; Harrison, 1983; Harrison et al., 1989; Mohie-Eldin et al. 1994). This shell (termed apoferritin) consists of an array of 24 polypeptide chains and has six openings ca. 1 nm in diameter which lead into the interior. The protein subunits are classified, on the basis of their molecular masses, as H (heavy) and L (light). The protein provides a means of exerting morphological control over the iron oxide core and reduces the (magnetic) interaction between the iron cores (Allen et al. 1998). XRD and point projection imaging suggest that the ferritin molecule has an overall diameter of 13 nm (Panitz & Ghiglia, 1982). A schematic picture of the ferritin molecule is shown in Fig. 17.2, left.

The iron core has the reddish brown colour of ferrihydrite and can be regarded as ferrihydrite associated with phosphate; the P/Fe mole ratio ranges from 0.05 to 0.25. The protein shell, together with the phosphate, stabilizes the ferrihydrite and prevents its transformation to a more crystalline, less readily soluble iron oxide as happens *in vitro* in the absence of stabilizers. The core is superparamagnetic at RT and the magnetic blocking temperature (T_B) for different ferritins decreases in the order: human spleen–limpet haemolymph–bacterial (Fig. 17.3). This reflects the degree of ordering which in turn, is associated with the P content (St. Pierre et al., 1986). TEM, XRD and HRTEM have shown that the structural order of the iron core varies in the same way as does that of ferrihydrite in abiotic environments. Well ordered,

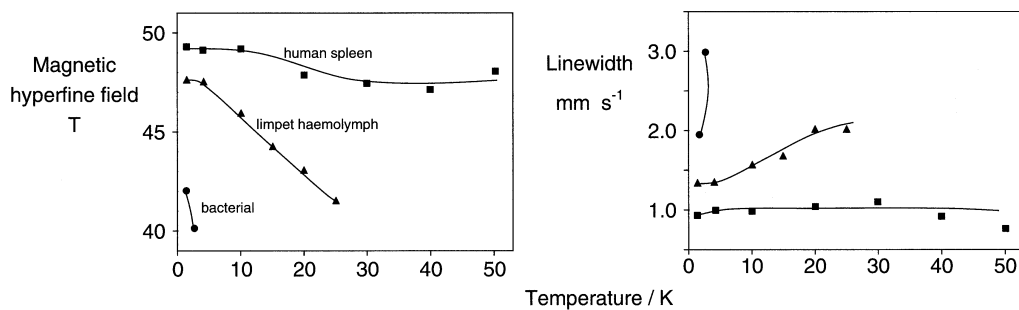


Fig. 17.3 Magnetic hyperfine field (left) and width of the outer lines of the sextets (right) obtained from Mössbauer spectra of ferritins, isolated from human spleen, limpet haemolymph and bacterial cells (*Pseudomonas aeruginosa*) as a function of temperature (Webb & St.Pierre, 1989; with permission).

single crystal ferritin has the XRD pattern of 6-line ferrihydrite, whereas the least crystalline material shows the XRD pattern typical of 2-line-ferrihydrite (Mann et al., 1986a). The degree of ordering increases from bacterial ferritin through limpet ferritin up to the best ordered material which is found in the human spleen. Electron nanodiffraction patterns show that the core consists of a single crystal which has essentially the hexagonal structure of ferrihydrite, although it has been suggested that minor amounts of hematite and maghemite-like structures are also present (Cowley et al. 2000). Isothermal, remanent magnetization and DC-demagnetization of native horse spleen ferritin were measured at 5K with a SQUID magnetometer by Allen et al. (1998).

There is a number of synthetic substitutes for natural ferritin and the properties of these have been compared with those of ferritin. The synthetic polysaccharide iron complex (PIC), has a magnetic blocking temperature of 48K (Mohie-Eldin et al. 1994). Iron-dextran complexes are used as a substitute for ferritin in the treatment of anaemia. The iron cores of these complexes consist not of ferrihydrite, but of very poorly crystalline akaganéite with magnetic blocking temperatures of between 150 and 290 K (Müller, 1967; Knight et al. 1999) which were lowered from 55K to 35 and 25K, if prepared in the presence of 0.250 and 0.284 Al/(Al + Fe), respectively (Cheng et al. 2001).

Formation of ferritin involves assemblage of the protein subunits to form the apoferritin shell which is then filled with the phosphated ferrihydrite core. The mechanism by which ferritin is filled and the iron core built up, has been investigated intensively *in vitro*. The experiments usually involved incubating apoferritin (from horse spleen) with Fe^{II} salts in the presence of an oxidant such as molecular oxygen. They showed that ferritin could be reconstituted from apoferritin and a source of Fe^{II} ; both the iron and the oxygen enter the protein shell, whereupon oxidation of Fe^{II} is catalysed by the interior surface of the protein shell (Macara et al., 1972).

It is thought that oxidation of Fe^{II} takes place at specific sites within the protein shell and is followed by inward migration and hydrolysis to form a stable core nu-

cleus (Webb et al., 1989). There appear to be two kinds of sites—a specific metal binding, oxidation site and a nearby anionic group of glutamate residues, which act together to ensure that ferrihydrite is deposited within the protein shell (Mann et al. 1993). The channels in the shell permit the passage of Fe^{II} , but are too narrow to accommodate Fe^{III} polynuclear species. As *in vitro* investigations of hydrolysis of Fe^{III} salts always produced ferrihydrite, it was assumed that it also formed *in vivo*.

An alternative mechanism has been proposed by Schneider (1988) who considers that ferritin could be also filled via a transient, mononuclear Fe^{III} species. This species is similar to Fe^{II} in size, but is more versatile in its interaction with the protein shell. Experiments have shown that as the pH of a system containing diferric-transferrin and ferritin was lowered very slowly from 7.5 to 5.0, monomeric Fe^{III} was released from the transferrin and redeposited in the ferritin (Glaus, 1989). Calculations of the iron flux across the cell membrane and estimates of the rates of interaction of the mononuclear species with ferritin and with the cell mitochondria indicated that the steady state concentration of the mononuclear Fe^{III} species would be sufficiently low for this species alone to enter the protein shell and be deposited as the iron core. Uptake of this species by the protein shell is about fiftyfold faster than the rate of hydrolytic polymerization or even of the dimerization of Fe^{III} ($t_{1/2} \approx 1$ vs. 50 ms). This hypothesis suggests an interesting direction for further research.

Ferritin can be converted *in situ* at 60°C to magnetoferritin by addition of Fe^{2+} ions (Meldrum et al. 1992). This process is an example of the use of the protein shell and other small volumes to synthesize nanominerals (Mann et al. 1993).

A second form of storage iron is *haemosiderin* (Weir et al., 1984). This is deposited in humans as a response to the condition of iron overload. Haemosiderin forms as insoluble granules with electron dense cores surrounded by a protein shell. It exists in two forms; primary haemosiderin is the result of iron overload due to excessive adsorption of iron in the gut, whereas the secondary form is caused by the numerous blood transfusions which are used to treat thalassaemia (a form of anaemia). Electron diffraction indicated that the iron core in primary haemosiderin is a 3-line ferrihydrite with magnetic hyperfine splitting only below 4 K and, in the secondary form, consists of poorly ordered goethite. As goethite is less soluble in ammonium oxalate buffer solution (pH 3) it has a lower intrinsic toxicity (Mann et al., 1988).

17.2.3

Magnetite

Biogenic magnetite was first found in the teeth of chitons (*Polyplacophora mollusca*) by Lowenstam in 1962¹⁾. It is also found in honey bees, homing pigeons (in the skull) and particularly in magnetotactic bacteria and algae (Gould et al., 1978; Walcott et al., 1979). In all these organisms, except chitons, magnetite appears to serve as a device for navigation. It is interesting to speculate on whether a similar directional device will be found in humans.

1) It is said that while holidaying in the Caribbean, Lowenstam became intrigued by the

black teeth of the chitons he observed on the beach and decided to examine them.

17.2.3.1 Magnetite in chitons' teeth

Chitons use their magnetite capped teeth for grazing purposes. The magnetite crystals, which are embedded in an ordered matrix of organic fibrils, display a range of sizes and morphologies (Towe & Lowenstam, 1967; Webb et al., 1989). In addition to magnetite, the mature teeth contain ferrihydrite, goethite or lepidocrocite and some calcium phosphate.

There are between 30 and 70 pairs of teeth along the radula, the first 5–7 of which are used for feeding. As they wear away, these teeth are discarded and the radula moves forward with the replacement teeth at the rate of one to two pairs a day. The complete tooth mineralization process is displayed in sequence along the radula, thus enabling each stage of development to be studied simultaneously. Tooth formation has four stages (Kirschvink & Lowenstam, 1979). The colourless, immature teeth consist only of the organic matrix; the second stage involves deposition of reddish-brown ferrihydrite in the organic matrix in the tooth caps and this is then converted to black magnetite. Finally, the magnetite thickens to a maximum value of 10 μm and, at the same time, the other minerals are deposited under the magnetite. The nature of the additional minerals depends on whether the chiton is a warm water or a cold water species.

The magnetite is considered to form from a ferrihydrite precursor by interaction of this phase with dissolved Fe^{II} ions (Kirschvink & Lowenstam, 1979; Lowenstam, 1981; Nesson & Lowenstam, 1985). The same mechanism operates for inorganic synthesis at around pH 7 (see chap. 13). Most probably the other iron oxides in the teeth form by a similar mechanism, but under conditions of slightly lower pH and/or higher redox potential. The separation of these minerals in time and space suggests local variations in growth conditions.

17.2.3.2 Magnetite in bacteria and other organisms

Biogenic magnetite is widespread in magnetotactic bacteria¹⁾. Such bacteria were first isolated in the sea by Blakemore in 1975. Subsequently, they have been found in anaerobic soils (Fassbinder et al., 1990) and in lakes (Vali & Kirschvink, 1991). Magnetotactic bacteria are a morphologically and physiologically diverse group of motile, Gram-negative procaryotes. Physiologically, they can be denitrifiers that are facultative, anaerobic, obligate micro-aerophiles and anaerobic sulphate-reducers. Of the various species, *Magnetospirillum magnetotacticum* has been studied in particular detail; subsequent comments refer mainly to this bacterium. Two other species which were discovered more recently are *Magnetospirillum gryphiswaldense* and *Magnetobacterium bavaricum*. The latter's cell is especially large (ca. 5 μm long) and contains four double rows of magnetosomes (Fig. 17.4). Magnetotactic bacteria are capable of sequestering large amounts of Fe from habitats relatively low in Fe (0.01–1 mgL^{-1}), i.e. against a large concentration gradient.

The magnetite crystals are well developed (euhedral), and this ensures that they act as single magnetic domains (SD) and produce remanent magnetization in sediments. The average number of magnetite crystals/cell in 220 cells of the microaero-

1) Magnetotaxis is orientation and migration along geomagnetic field lines.

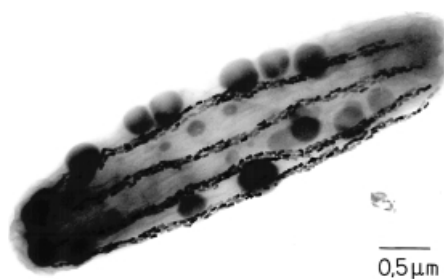


Fig. 17.4 *Magnetobacterium bavaricum* from lake Chiemsee, Bavaria with four double rows of bullet-shaped magnetosomes (courtesy Dr. M. Hanslick, Munich)

phyllic bacterium *Magnetospirillum gryphiswaldense* was 12 (Bäuerlein, 2000), but up to 60 have been counted in some cells (Schüler, 2000). From a 30 μM Fe(III)citrate solution and at low O₂ concentration (2–7 μM O₂), *M. gryphiswaldense* produced up to 60 magnetite crystals per cell, 42–45 μm in size (Schüler & Bäuerlein, 1997). The average length and width of 150 crystals from magnetococcoid bacterial cells was 100 nm and 62 nm, respectively, yielding a mean width-to-length ratio of 0.63 (Towe & Moench, 1981). In comparison with synthetic magnetites of similar size, produced by oxidizing a FeSO₄ solution at 85 °C with KNO₃ (Schwertmann & Cornell, 2000), the bacterial magnetite usually has a narrower size distribution (Devouard et al. 1998). Schüler (2000 a), therefore, suggested biotic formation as a possible means of producing uniform, nano magnetite for industrial purposes. In projection, the crystals are hexagonal, rectangular, cubic or bullet-shaped (Fig. 17.5). The mostly isometric crystals are regarded as having cuboctahedral morphologies based on the octahedral and elongated hexagonal prism which can be derived from various combinations of the isometric {111}, {100} and {110} forms (Mann & Frankel, 1989; Devouard et al. 1998). Mössbauer spectra have shown that the composition is close to stoichiometric although in some cases, a reduction of the unit cell size may indicate partial oxidation of Fe^{II} in the structure (Mann & Frankel, 1989). It was suggested that small amounts of Ti may also be located in the structure (Towe & Moench, 1981), but usually the chemical purity is remarkably high.

The magnetite crystals are surrounded by an intra-cytoplasmic membrane and this combination is termed a *magnetosome* (Balkwill et al. 1980; Mann & Frankel, 1989) (Fig. 17.6; right). The magnetosomes give the bacterial cells a permanent dipole moment of ca. $6 \cdot 10^{-17}$ J T⁻¹ per crystal and this enables the organism to navigate in the earth's magnetic field. In most cases, the magnetosomes are arranged in chains along the motility axis (i.e. parallel to [111]) so as to increase the magnetic moment (Figs. 17.4 & 17.5). The magnetosome membrane is about 8–12 nm thick. It seems to be preformed and, thus, determines the size of the magnetite crystal (Schüler, 1999; 2000).

Thomas-Keprta et al. (2000) summarized the six properties of biogenic magnetite which clearly differentiate it from magnetite formed inorganically and at the same time optimize the magnetic moment and thus, the efficiency with which the bacteria move in the geomagnetic field. These properties are: single-domain size, chemical purity, structural perfection, association into chains, distinct crystal habit and crystallographic direction of crystal elongation. This optimisation is thought to be the result

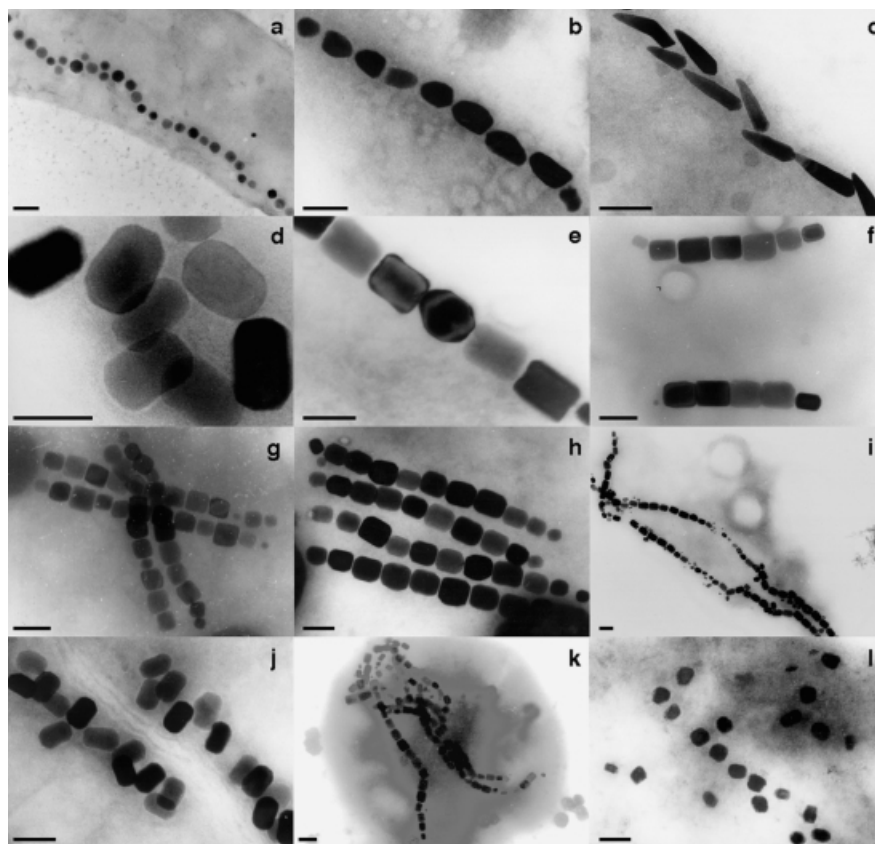
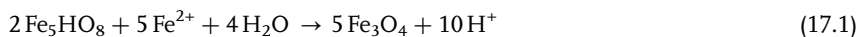


Fig. 17.5 Shapes and intracellular arrangement of magnetosomes in various magnetotactic bacteria: cubooctahedral (a), bullet-shaped (b,c), prismatic (d-k) and rectangular (l) magnetites arranged mostly in one or multiple chains, (Bar = 0.1 μm). (Schüler, 1999; with permission).

of Darwinian selection. The magnetosomes enable the bacteria to move in the geomagnetic field (magnetotaxis), possibly in order to avoid high, potentially toxic, oxygen tension.

The details of enzymatic magnetite formation in bacteria, especially the valence and chemical form in which the Fe enters the cell, are still not fully understood. At low oxygen concentrations in the bacterial habitats dissolved Fe may exist in bivalent form, but Fe added as a soluble Fe^{III} complex, such as Fe^{III} citrate (Schüler & Bäuerlein, 1996) can also function as an Fe source. Within the cell, part of the Fe will then form a highly reactive Fe^{III} oxide, probably ferrihydrite, which in turn, reacts with the dissolved Fe^{2+} to form magnetite (Mann et al. 1989) by a via-solution process (Fig. 17.6):



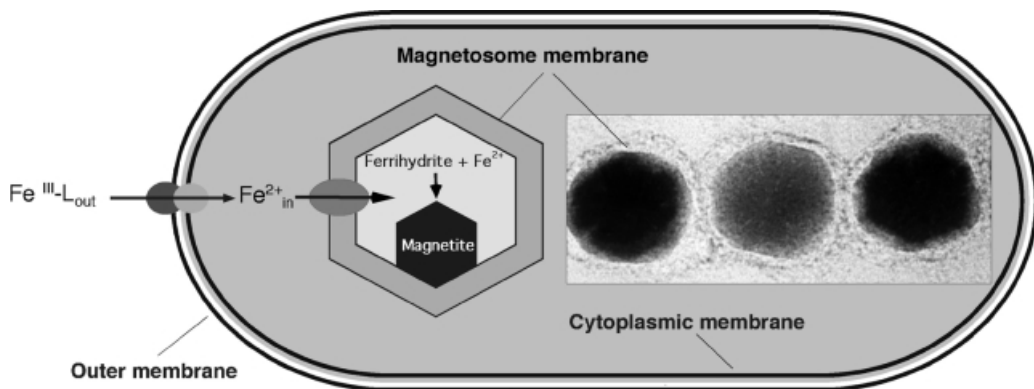


Fig. 17.6 Left hand side: Model for the formation of magnetite in a *Magnetospirillum* species. “L” stands for an organic ligand. The oval forms represent specific Fe transport proteins, Right hand side: Three magnetosomes encapsulated by a membrane (slightly modified) (Courtesy D. Schüller; MPI Bremen; see Schüller, 1999; with permission).

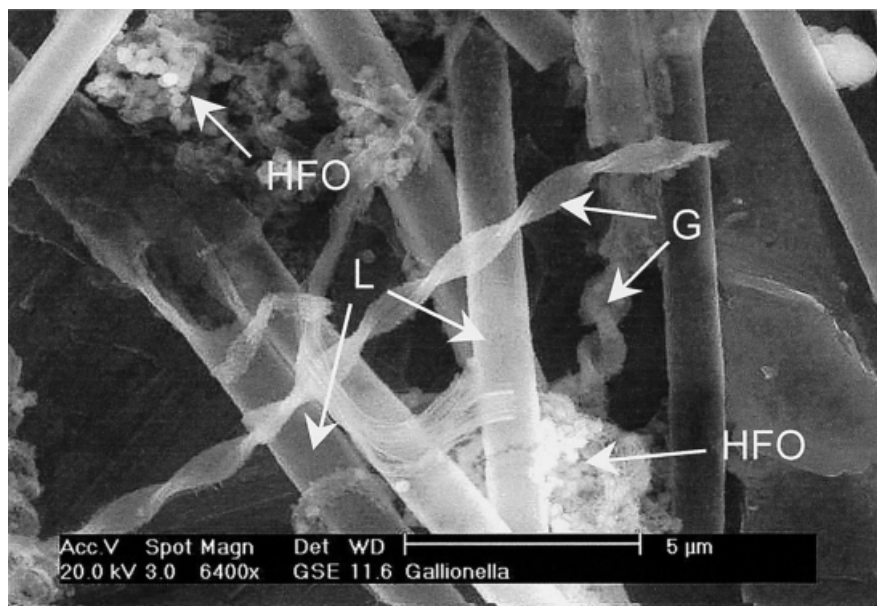


Fig. 17.7 Ferrihydrite (HFO) precipitated in the neighbourhood of stalks of *Leptotrix* (L) and *Gallionella* (G) 195 m underground at the Strassa Mine, Sweden (Courtesy F.G. Ferris).

Ferrihydrite has indeed been found in association with magnetite in *Magnetospirillum magnetotacticum* (Frankel et al., 1983). It seems essential that the cell solution is sufficiently buffered to maintain a neutral pH and thus ensure that the solubility product of magnetite is always exceeded. This is a reaction which easily takes place in a purely inorganic system at ambient temperature (see chap. 14). Lepidocrocite has also been suggested as a magnetite precursor (Abe et al. 1983).

With *M. gryphiswaldense*, Schüler and Bäuerlein (1996) recorded an Fe uptake rate from Fe^{III} citrate of $0.86 \text{ nmol min}^{-1} \text{ mg dry weight}^{-1}$ and suggested that the major portion of Fe is taken up in an energy-dependent process possibly by a reductive step (Schüler, 1999). Fukumori et al. (1997) proposed that the dissimilatory nitrite reductase of *M. magnetotacticum* may function as an Fe^{II} oxidizing enzyme. Later, Fukumori (2000) suggested an Fe^{III} quinate complex as the source of Fe which is subsequently reduced in the cell in a microaerobic environment at about neutral pH by the iron reductase NADH (an assimilatory enzyme).

Although the mechanism in eq. 17.1 is considered to be similar to that proposed for chitons (Mann & Frankel, 1989), Lowenstam and Weiner (1989) suggested that the presence of the organic membrane together with the preferred orientation and single domain nature of the crystals indicate that biomineralization in bacteria is more complicated than in chiton's teeth and involves matrix mediation, i.e. the organic matrix directs nucleation and crystal size and the magnetosomes are boundary organized. In *M. gryphiswaldense*, which can be cultivated in the laboratory, genes have been identified which direct the production of the protein shell encapsulating the SD magnetites and these have no known homologue in any non-magnetic organism (Grünberg et al. 2001). The remarkably uniform shape and size of the bio-magnetites appears then to be linked to the size and shape of the protein shell of the magnetosome. Probably the magnetosomes have specific functions in the accumulation of iron, nucleation of the oxide and E_h and pH control.

Recently a new route for intracellular magnetite/maghemite formation was suggested by Glasauer et al. (2002); in this *Shewanella putrefaciens*, a dissimilatory Fe-reducing bacterium, produces Fe^{2+} extracellularly from added 2-line ferrihydrite under anaerobic conditions. After entering the cell the Fe^{2+} forms a cubic phase, probably magnetite/maghemite. The crystals were several tens of nm in size and surrounded by a membrane similar to that in magnetosomes, but not arranged in chains as in magnetotactic bacteria. The high reactivity of ferrihydrite appeared to be essential for the Fe^{II} and magnetite formation since neither goethite nor hematite reacted in the same way.

Magnetotactic algae have been identified in brackish sediments in Brazil (Torres de Araujo et al., 1986). The magnetite crystals are arrow-headed and are arranged in chains parallel to the long axis of the cell. Cubo-octahedral magnetite crystals about 4 nm in size were also identified in the leaves and stems of a grass (*Festuca spec.*) (Gajdardziska-Josifovska et al. 2001).

Biogenic magnetite may persist once the organism that produced it has died and may, therefore, contribute to the natural magnetic remanence of sediments (Stolz et al., 1986). The discovery in a calcareous Martian (?) meteorite found in Antarctica, of magnetite crystals with properties very similar to these biogenic magnetites, sup-

ports the idea of the existence of life on the early Mars (Thomas-Keprta et al. 2000). This conclusion drawn solely from the crystal shape has, however, been challenged (see chap. 15).

17.3

Biotically induced formation

Iron oxides are also formed extracellularly by various organisms (Lundgren and Dean, 1979; Fischer, 1988). Figure 17.7 shows Fe oxide aggregates (probably ferrihydrite) in the immediate neighbourhood of the two Fe oxidizing species, *Gallionella ferruginea* (G) and *Leptothrix ochracea* (L). This type of extracellular Fe oxide formation is called *induced* formation and refers predominantly to the oxidation of Fe^{2+} in aqueous systems. There is increasing interest in this process because it is quite common in water and soil systems where the biogenically formed Fe oxides play an important role in the retention of environmentally significant compounds. Whereas the reduction of Fe in these systems usually occurs biotically, oxidation of Fe^{2+} requires biogenic activity only under acid conditions or at a Eh too low for the abiotic oxidation. In each case, oxygen serves as an electron acceptor. Most investigations into the formation of iron oxides as a result of bioactivity have concentrated on the biochemistry of the processes involved. Only recently has greater interest in the characteristics of the iron oxides formed, developed.

Induced, extracellular Fe oxide formation is observed in bacterial colonies isolated from natural Fe containing waters (Fitzpatrick et al. 1992) and in laboratory cultures (Fortin & Ferris, 1998); the Fe oxides may often completely coat or fill the cells (Fig. 17.8). The Fe oxides of encrusted cells of *Gallionella ferruginea* and other species in deep ground waters contained between 360 to 480 g Fe/kg, but also a range of other elements such as Cs, Sr, Mn, Zn, Pb, P and U (Ferris et al 1999). Si-containing, Fe-rich precipitates (goethite and ferrihydrite(?)) around bacterial cells from the Amazon river system (Konhauser et al. 1993), from hot springs in Iceland (Konhauser and Ferris, 1996) and from a spring in an active volcano in Kyushu, Japan (Tazaki, 2000; see Plate 15) have also been reported. It is speculated that such formations have also occurred in the geological past and have led to such iron ore deposits as the banded iron formations (Chap. 15). Warren and Ferris (1998) suggested that the surfaces of bacterial cells provide sites (functional groups) for oxide nucleation. This has been demonstrated in a pure Fe^{III} system where a variety of bacteria (*Pseudomonas*, *Bacterium*) induced removal of Fe^{III} from solution at a pH at which no precipitation could occur in the absence of bacteria. An atomic force microscope was used to show that the adhesive forces between *Escherichia coli* cells and the surface of goethite at distances of up to 400nm separation were of the order of several nN (Lower et al. 2000).

How organisms induce oxide formation depends upon the degree to which iron participates in their physiological processes. Organisms which precipitate iron oxides extracellularly are either autotrophic or heterotrophic. *Autotrophic* organisms obtain energy for metabolism by oxidation of Fe^{II} . This biotic oxidation reaction is

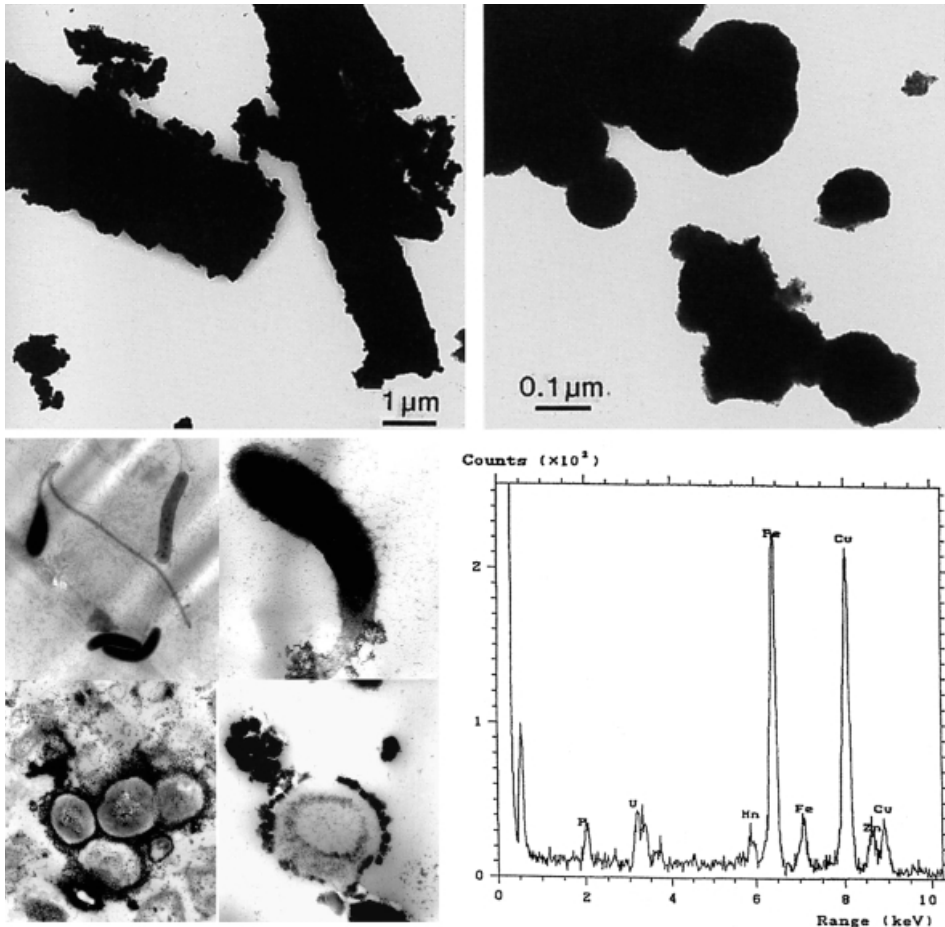


Fig. 17.8 Upper: Bacterial relics filled with ferrihydrite, probably from *Leptothrix* (left) and *Gallionella* (right), formed by rapid oxidation of ferri-ferrous waters of drainage ditches (Süsser & Schwertmann, 1983; with permission). Lower: Accumulation of Fe oxides (ferrihydrite?) around bacterial cells collected from a deep water

source at the Äspö Hard Rock Laboratory near Oskarshamn, Sweden and an EDX spectrum of these. Bars = 0.5 µm (The Cu peaks are from the copper grid) [Reprinted with permission of Taylor and Francis Ltd (<http://www.tandf.co.uk/journals>) from Ferris et al., 1999, *Geomicrobiol. J.* 16, 181].

termed “iron respiration”. One intensively studied bacterium which comes into this class is the autotrophic acidophile, *Thiobacillus ferrooxidans*, (filamentous) which can oxidize sulphur and sulphide as well as Fe^{II} . This organism is aerobic and operates most effectively at temperatures of between 30–45 °C. It occurs mainly in the so-called acid sulphate soils (Fanning and Burch, 1997), in acidic, oxygenated waters originating from sulphide weathering, either natural or at mine sites (acid mine waters) and in acidic hot springs. It oxidizes Fe^{II} at a rate which is several orders of

magnitude greater than would occur in an inorganic system; in fact at pH 3, oxidation in the absence of the bacteria is so slow as to be non-existent.

The kinetic hindrance of Fe^{2+} oxidation at low pH in an abiotic system is overcome by enzymes produced by the bacterium (Fig. 17.9). Basically, the electron released from Fe^{2+} is transferred to oxygen via the various cell membranes through several acceptors (e.g. cytochromes) to reduce oxygen; the actual Fe from which the oxide is formed does not enter the cell (Ghiorse & Ehrlich, 1992). During this process, some energy is conserved in ATP by a charge separation process (chemi-osmosis) and is used for endergonic metabolic processes.

A second group of microbes oxidizes Fe^{2+} at under close to neutral pH. Best known are the twisted stalks of *Leptothrix ochrea* and the tube-like shafts of *Gallionella ferruginea* (Fig. 17.8) (Fitzpatrick et al., 1992; Ferris et al. 2000). Other organisms in this class include *Siderocapsa*, *Toxothrix trichogenes* (Chukhrov et al., 1973 a), *Metallogenium*, *Siderococcus limoniticus* (Dubinina & Kuznetsov, 1976) and *Hyphomicrobium* (Jannasch & Wirsén, 1981) (for a list of bacteria see Fischer, 1988). These species are micro-aerophilic and oxidize Fe^{2+} at low Eh where abiotic oxidation is very slow. Iron-oxidizing organisms are widespread in various natural and anthropogenic Fe containing environments. Examples are cold and hot springs, reductomorphic soils, lakes, water courses and artificial drainage systems.

Heterotrophic organisms (e.g. bacteria [*Bacterium metallogenium*, *B. pedomicrobium*], actinomycetes and fungi) obtain energy by oxidation (decomposition) of organic matter. Such organisms may induce oxidation of Fe^{II} directly or may interact with Fe^{II} or Fe^{III} -organic complexes.

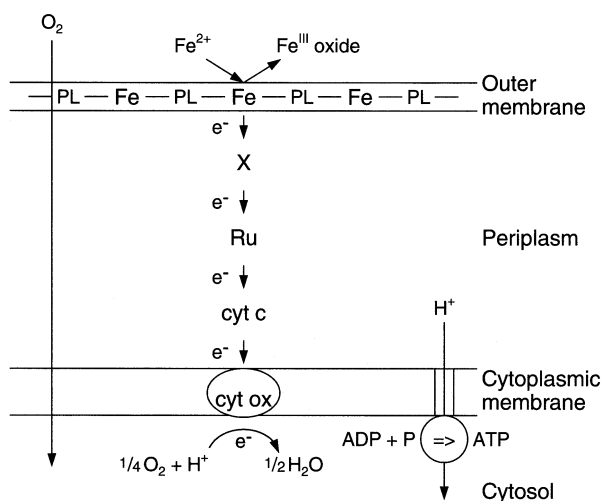


Fig. 17.9 Model of the mechanism of Fe^{2+} oxidation by *Thiobacillus ferrooxidans*. PL-Fe: phospholipid bound Fe; x: enzyme (unidentified); Ru: rusticyane, a Cu-containing protein; cyt c: c-type cytochrome; cyt ox: cytochrome oxidase complex; ATP: adenosine 5'-triphosphate (Ghiorse & Ehrlich, 1992; with permission).

Another example of biotically induced Fe oxide formation is found in the rhizosphere of the higher plants growing in strictly anaerobic, i.e. water saturated, soils at low Eh. This is frequently observed with rice plants (*Oryza sativa*) the roots of which are often surrounded by ochreous precipitates (Trolldenier, 1988), but other species show the same phenomenon. For example, *Juncus bulbosus* (rush) and *Eriophorum angustifolium* growing in an acid mine water lake, emit molecular oxygen into the rhizosphere to oxidize and precipitate Fe and thereby prevent intoxication by iron (Chabbi, 1999 & pers. com.). However, due to their high capacity for binding phosphate, these rhizospheric Fe oxides interfere with the phosphate uptake by the plant (Zhang et al. 1999). On the other hand, they shift the electron flow from the formation of methane (methanogenesis) to iron reduction, thereby reducing CH₄ production in such soils (Frenzel et al. 1999).

With regard to the mineralogical nature of the biogenic Fe oxides, the conditions of formation often do not favour the better crystalline forms. Low temperatures, rapid formation, and interfering compounds, such as organics and Si, are the main reasons for this poor performance (see chap. 15). Lepidocrocite formation from Fe²⁺ was hindered and ferrihydrite formed instead, in the presence of the bacterial cells (*Bacillus subtilis* and *B. licheniformis*) (Mavrocordatos and Fortin, 2001). The oxidation of Fe²⁺ by O₂ at pH 7 by *Bacillus subtilis* and *Escherichia coli* led to lepidocrocite as in inorganic systems, although the crystallinity, especially that associated with cells may be somewhat lower (Chatellier et al. 2001).

In strongly acidic waters, originating from pyrite oxidation, incompletely hydrolysed Fe^{III} phases, such as the jarosites and schwertmannite (Plate 15.V) predominate as long as the pH is below 4. At higher pH, ferrihydrite often predominates, but goethite (Huggins et al., 1980; Chabbi, 1999) and lepidocrocite also occur. Ferrihydrite was identified in fresh water springs (Plate 15.III), lakes, soils and in artificial drainage systems (Plate 15.IV) (Chukhrov et al., 1973a; Tipping et al., 1981; Murad, 1982; Süsser & Schwertmann, 1983; Milnes et al., 1992; Fitzpatrick et al., 1992). Bacterial cells or cell shaped bodies (often stalk- or sheath-like) frequently occur in these deposits. In a hydrothermal vent on the Southern Explorer Ridge (NE Pacific), the oxides coating bacterial surfaces consisted of isodimensional particles < 20nm in size, and fine, 20–100 nm long filaments made up of very small spherical particles. According to the XRD peaks at 0.15 and 0.25 nm, they were 2-line ferrihydrite probably containing Si (Fortin et al. 1998). In a laboratory study with a range of non-iron oxidizing bacteria (*Pseudomonas*, *Bacterium*), formation of 2-line ferrihydrite from Fe^{III} nitrate solutions was enhanced over that in a purely inorganic system (Warren and Ferris, 1998). A P-rich iron oxide, probably ferrihydrite, was identified in the biofilm of Montacuta, a marine bivalve (mollusk) (Gillan & De Ridder, 2001).

Large amounts of extracellular, fine grained magnetite are formed by an organism (designated as GS-15) under aerobic conditions (Lovley et al., 1987). The process, which involves coupling of organic matter oxidation with reduction of Fe^{III}, has been simulated in the laboratory. Extracellular, single-domain magnetite crystals ca 50 nm in size formed within 24 hr when a thermophilic, fermentative, anaerobic bacterium (TOR-39) was grown at 65°C in a 2-line ferrihydrite suspension, with an Eh of –0.3 V and a pH of 7 (Zhang et al. 1998). The reaction is analogous to that between ferrihydrite and Fe²⁺ in an inorganic system (see chap. 14).

18

Products of iron metal corrosion

18.1

General

“What iron oxide phase will form when iron corrodes under a particular set of conditions?” This question is often asked and the present chapter is concerned with answering it. Before considering the products of corrosion, however, a background to the process is required. The corrosion of iron and steel is, of course, a vast field. Detailed information may be found in the books by Uhlig (1963), Evans (1968) and West (1980). Here, a brief summary of the main aspects is provided.

Although iron corrodes under an immense variety of conditions, there are, basically, only two mechanisms involved, namely electrochemical corrosion and (hot gas) oxidation.

18.2

Electrochemical corrosion

Upon exposure to water, iron corrodes, i.e. dissolves. This type of corrosion is an electrochemical reaction in which iron acts as the anode, i.e. is oxidized;

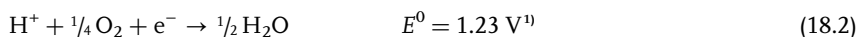


E^0 is the standard equilibrium potential, i.e. the potential corresponding to unit activity and RTP. The dissolution reaction leads to the development of an electrical double layer at the iron-solution interface. The potential difference of the Fe/Fe²⁺ half cell cannot be measured directly, but if the iron electrode is coupled with a reference electrode (usually the standard hydrogen electrode, SHE), a relative potential difference, E , can be measured. This potential is termed the single potential of the Fe/Fe²⁺ electrode on the scale of the standard hydrogen couple H₂/H⁺, the standard potential of which is taken as zero. The value of the equilibrium potential of an electrochemical cell depends upon the concentrations of the species involved.

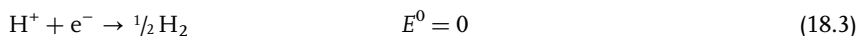
The half reaction for iron dissolution proceeds until equilibrium is reached. Further corrosion of iron requires that the single potential is raised to some nonequi-

librium value. The extent of the change of the potential is termed the overpotential and the greater its value, the greater the tendency to corrode. The standard single potential of iron can be increased by the application of an external electro motive force to the electrode (e.g. during anodic passivation), or by the presence of an oxidizing agent such as oxygen.

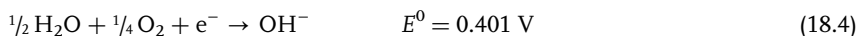
Electrochemical corrosion involves one of three major cathodic reactions. The first occurs in aerated, acid to neutral solutions (e.g. in seawater and under conditions of atmospheric weathering) and involves reduction of oxygen,



In deaerated, acid solutions, protons are the oxidizing agents, i.e.,



In aerated, alkaline solutions oxygen is again reduced, i.e.



The reaction produces hydroxyl ions which react directly with the Fe^{2+} ions to produce an oxide precipitate. The combined anodic and cathodic reactions form the corrosion cell, the electrochemical potential of which lies between the single potential of the two half reactions. This mixed potential is termed the corrosion potential, E_{corr} , and for corrosion to proceed beyond the equilibrium state, the corrosion potential must be more positive than the equilibrium single potential of iron. For iron in water at pH 7 and with $[\text{Fe}^{2+}] = 10^{-6} \text{ M}$, for example, the potential of the anodic reaction is,

$$E_{\text{Fe}} = E^0 + \frac{RT}{zF} \ln [\text{Fe}^{2+}] = -0.44 + 0.03 \log [\text{Fe}^{2+}] = 0.62 \text{ V} \quad (18.5)$$

The cathodic reaction is,

$$E_{\text{O}_2} = E^0 + 0.015 \log (a_{\text{O}_2}) - 0.059 \text{ pH} = 0.8 \text{ V} (a_{\text{O}_2} = 0.2) \quad (18.6)$$

hence

$$E = E_{\text{O}_2} - E_{\text{Fe}} = 1.42 \text{ V} \quad (18.7)$$

E is the driving electromotive force for the corrosion reaction.

The rate at which corrosion occurs is expressed as the current density (A m^{-2}), i.e. the ionic flux across the electrical double layer of the metal and at equilibrium, it is termed the exchange current density. The Tafel equation relates the exchange current density to the charge transfer overpotential.

- 1) As potential depends upon the concentration of the species in the cell, E^0 must be modified for deviations from unit activity to obtain E .

One of the best known examples of electrochemical corrosion is atmospheric rusting. For this to occur, a certain critical relative humidity of between 60–80% or higher (depending upon whether salts are present) is required. At such a relative humidity, every object is covered with a coherent film of water which serves as an electrolyte. Electrochemical corrosion also occurs when an iron object is partly or completely immersed in water.

When oxygen is the oxidizing agent, differential aeration can lead to separation of the anodic and the cathodic reactions with the corrosion product being deposited some distance away from the point at which the iron actually corrodes. In such a case, rust is said to “travel” and cannot form a protective layer. A classic illustration of this situation is the drop of salt solution on a sheet of iron (Evans, 1963); phenolphthalein and potassium hexacyanoferrate are used to indicate the cathodic and anodic regions, respectively. During corrosion, a blue patch corresponding to the release of Fe^{2+} ions and formation of Prussian blue, develops in the centre of the salt drop, whereas the cathodic region appears as a circle of pink (due to production of OH^- ions) near the edge of the droplet. Between the anodic and cathodic regions, a ring of yellow-brown rust precipitates as a result of interaction between outward migrating Fe^{2+} ions and inward moving OH^- ions, followed by oxidation.

Pourbaix diagrams (Pourbaix, 1963) indicate graphically the conditions of redox potential (Eh) and pH under which different types of corrosion behaviour may be expected. These plots of potential vs. pH indicate the phase and species in equilibrium with iron under various conditions (see Chap. 8). The solid phases indicated are those that are thermodynamically the most stable; owing to kinetic factors other phases may be present during the initial stages of the corrosion process. What the different regions show, however, are the predominant oxidation states to be expected. The value of such a diagram is that it can be simplified to indicate the three domains of corrosion behaviour, i.e. where the iron is immune (does not corrode), where corrosion takes place and where iron is passive (Fig. 18.1).

Corrosion of iron tends to start at an Eh of -0.6 V. At lower Eh, iron is *immune*, i.e. corrosion cannot occur and the iron is thermodynamically stable in water; any Fe^{2+} in solution under these conditions would be deposited as the metal. As the po-

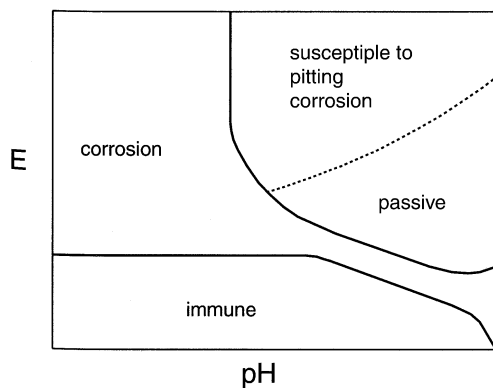


Fig. 18.1 Schematic Pourbaix diagram for iron in sea water at 25 °C showing the domains of corrosion behavior (West, 1980, with permission).

tential increases (due either to the presence of an oxidizing agent or the application of an external emf), iron corrodes. The *corrosion domains* correspond to the areas where Fe^{2+} and Fe^{3+} are present. The *passive domain* has attracted considerable interest owing to the immunity to corrosion that iron attracts in this region. It corresponds to conditions under which corrosion would be expected to be accelerated, but instead decreases to a negligible value, owing to the formation on the surface of iron, of a barrier to the transport of reacting species; this barrier is the stable oxide film.

Passivity can be induced by immersion of iron in a concentrated solution of HNO_3 . This treatment induces formation on iron of a long lived, protective film which resists dissolution in dilute acid. Alternatively, iron may be passivated anodically; this involves application of a high enough current density to an iron electrode being held in an electrolyte (acidic, basic or salt) solution. At low current densities, corrosion is accelerated as the current density rises, but when the applied potential reaches the passivation value, the current density and the rate of dissolution drop sharply owing to formation to a thin protective film of oxide on the iron. This passive layer is electrolytically conducting, so very slow corrosion can still proceed (Brusic, 1979). The film can be thickened to some extent by subjecting the electrode to very fast oxidation/reduction cycles (Froelicher et al., 1983); thicker films can be analysed more readily. Once the applied potential is removed, the passivity of the iron is usually short-lived – the oxide film dissolves and corrosion proceeds. For Fe-Cr alloys, passivity may also be lost if the applied potential is increased to very high values (0.9 V). In this *transpassive* region, the protective film (which is enriched in chromium) breaks down owing to oxidation of Cr^{III} in the film to Cr^{VI} in solution. Transpassive dissolution of pure iron to a ferrate $^{\text{VI}}$ species has been reported at 0.65–0.85 V in NaOH (Beck, et al., 1985).

The passive region may extend over a wide range of redox potential and pH. Pourbaix diagrams can be constructed for different corrosion conditions, for example, iron and alloyed steels in various electrolytes. In such systems, the extent of the passive domain can be quite different from that observed for the iron/pure water system. In the presence of chloride ions which are extremely aggressive towards the protective film, the passive region shrinks considerably. Pourbaix diagrams provide a good guide to what corrosion behaviour is thermodynamically possible. What is actually observed, however, depends on a wide range of chemical, physical and hydrodynamic factors.

18.3

High temperature oxidation/corrosion in gases

At temperatures ranging from below room temperature to temperatures of up to 1000°C , iron reacts chemically with the oxygen of the air to form a surface film of oxide. The films formed at room temperature (at relative humidities below the critical value) are only a few Å thick and hence are invisible, but at higher temperatures, thick scales are produced. This type of corrosion involves an oxidation/reduction re-

action, but unlike electrochemical corrosion, occurs in the dry state. The reaction takes place in the oxide layer instead of in the electrolyte and the limiting factor is the availability of oxygen, not of moisture.

The formation of an oxide layer is thermodynamically favourable and kinetically rapid at room temperature, but as the temperature rises, the free energy of oxide formation (originally negative) increases to the point where the metal, oxide and oxygen are in equilibrium. At temperatures above this equilibrium value, and if the oxygen partial pressure is low enough, the oxide can decompose.

For oxidation of iron to occur at high temperatures, the oxygen partial pressure must be above that of the dissociation pressure of the appropriate corrosion products. For example, at ca. 700 °C, an oxygen partial pressure of greater than 10^{-15} Pa is required for wüstite to form. In air, of course, this condition is readily satisfied, at least initially. As oxidation continues and the film thickens and becomes coherent, an oxygen gradient across the film is established and the composition of the corrosion layer changes.

On a freshly cleaned iron surface, oxidation is initially fast, but as the oxide layer grows, it acts as a barrier between the interacting species and the reaction rate soon falls. The higher the temperature, the thicker the film before the fall in oxidation rate becomes significant.

At high temperatures the oxidation rate k is, initially, rectilinear (i.e. the interfacial reaction is rate-determining), i.e.

$$x = kt + m \quad (18.8)$$

where x is the thickness of the film, t is the time and m a constant. With time and increasing film thickness and coherency, the kinetics change and the reaction is now controlled by outward diffusion of metal ions and electrons across the film, together with possible migration of anions inwards (Fig. 18.2). A parabolic (Wagner's) law is now obeyed, i.e.

$$x^2 = kt + m \quad (18.9)$$

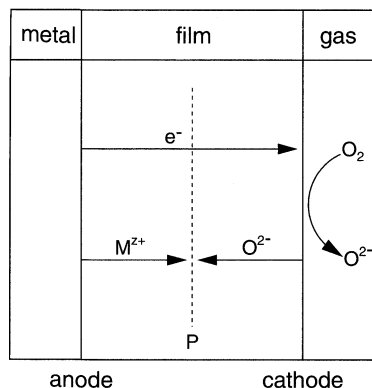


Fig. 18.2 Schematic representation of oxidation of iron. P = plane of growth (West, 1980, with permission).

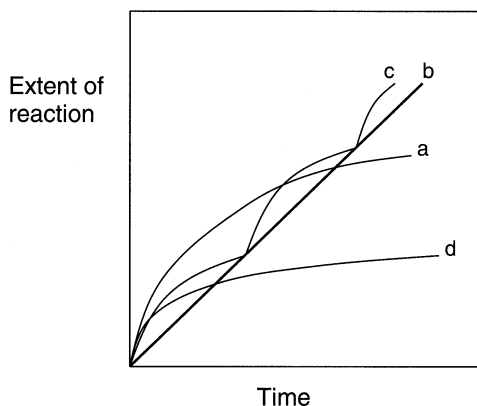


Fig. 18.3 Plots of the growth “laws” of oxidation: a) parabolic, b) rectilinear, c) quasi-rectilinear, d) logarithmic (West, 1980, with permission).

This parabolic law, which indicates that diffusion is rate-limiting, is of overwhelming importance for scale formation. Wagner (1933) showed that the parabolic scale constant (and hence, rate of oxidation) can be calculated using the enthalpy of formation of the corrosion product, the electrical conductivity of the protective film and the transport number of the ions and electrons in the film.

The parabolic law is obeyed only over the (limited) temperature range over which a continuous oxide layer forms. Whether or not the oxide layer is coherent depends upon the ratio of the volume of oxide formed to the volume of iron corroded to produce the film. For iron, the ratio (the Pilling-Bedworth ratio) is 2.1 which indicates that the oxide occupies a larger volume than does the amount of metal consumed. The film is, therefore, under compression and as it thickens (> 10 nm), stresses and flaws develop. When this happens the parabolic law no longer operates and growth may be either quasi linear or logarithmic. The different types of possible kinetic plots are shown schematically in Figure 18.3. Low temperature (< 400 °C) oxidation of iron follows a logarithmic law, $x = \ln(kt)$. Obedience to this law is thought to be due to reduced electronic conductivity as the film thickens, rather than to cracks in the film.

18.4

Other forms of corrosion

The two basic types of corrosion discussed above form the general background to the subject. How, and to what extent, any particular object or structure corrodes also depends on other factors, in particular, on whether corrosion is uniform or not and on the effects of mechanical strain. These factors are interactive and in combination, their individual effects can be enhanced.

Uniform corrosion, which involves progressive and uniform thinning of the metal, is the simplest and commonest form of corrosion. With appropriate engineering design, it can be controlled relatively easily.

Nonuniform corrosion is more complicated and difficult to control. It has a number of causes. The most frequent type of nonuniform corrosion is *crevice attack* – a localized form of attack in which some form of geometrical discontinuity influences the availability of one or more of the reactants. Among the discontinuities around which such attack occurs are bolts, holes, joints and bend in pipes (e.g. the exhaust pipe of a car). *Bimetallic* corrosion is also nonuniform and occurs when two dissimilar metals, one of which corrodes preferentially, are joined together. Selective attack also occurs along *grain boundaries* in iron. It can cause the whole grain to fall out, often with disastrous effects on the structure. A related form of nonuniform corrosion is *graphitization* or spongiosis observed with grey cast iron. In this type of attack, the ferrite (α -Fe) and perlite (α -Fe/Fe₃C) sections of the iron corrode, whereas the graphite structure remains intact. A further, most destructive and common form of attack is *pitting* corrosion. This is associated with differential aeration and occurs when the metal is covered by a protective coating with pores or defects. The depth of the pit is usually greater than its diameter. The presence of chloride ions promotes extensive pitting in stainless steel structures in chemical plants.

An equally important aspect of the corrosion process is the effect of mechanical stress. Such stress, combined with local electrochemical corrosion can cause rapid an unexpected cracking in equipment such as reactors and piping, often at stresses well below those that would cause rupture in the absence of corrosion. Stress corrosion is particularly important because, although it does not produce large quantities of corrosion products, it leads to catastrophic failure of structures (e.g. bridges and indoor swimming pools) in unexpected ways. Stress corrosion cracking can also damage otherwise protective surface films.

18.5

The products of corrosion

All the major iron oxides have been identified in the corrosion products of iron and steel. The general relationships between these phases formed and the conditions under which they have been deposited are discussed in Chapter 13 and 14: they apply to situations under which corrosion occurs (Johnston et al., 1978). Unfortunately, information about the environmental parameters at the corrosion site is often scarce. Nevertheless, the few conclusions which can be drawn are in accord with those in the earlier chapters. The frequent occurrence of green rust, magnetite and lepidocrocite, for example, is associated with an ample supply of Fe²⁺ ions. In addition, the presence of magnetite probably indicates a pH > 7. In aqueous systems, hematite usually occurs only in corrosion products formed at elevated temperatures (> 250 °C), for example in the cooling coils of nuclear power plants (Blesa et al., 1978). As it has a high thermodynamic stability, goethite can be a primary precipitate as well as a transformation product of other phases. Lepidocrocite transforms to goethite in rust formed in both temperate and tropical conditions (Hiller, 1966; Furet et al., 1990) and, under the influence of high levels of Fe²⁺, goes to magnetite. Due to the often combined presence of Fe²⁺ ions and alkaline conditions, green rusts are

common corrosion products and depending upon the level of carbonate and sulphate ions in the system, they transform either to goethite or to lepidocrocite. Formation of akaganéite-containing rusts requires the presence of chloride ions.

Both rust and oxide scales are usually mixtures of iron oxides with other Fe (e.g. siderite) and non-Fe compounds (CaCO_3). In some cases there is a more or less random mixture of components, whereas in others, the different oxides are arranged in layers to form duplex or triplex scales. Layer-type rust arises as a result of potential or chemical gradients across the film. As these gradients vary with film thickness, the composition of the rust changes with the distance from the metal. On the whole, if Fe^{III} and Fe^{II} are present, the oxide containing Fe^{II} is found in the inner layer of the rust.

The composition of the rust/scale is most reliably determined using X-ray diffraction. In many cases, however, the oxide film is too thin for this technique to be applied and identification of the phases requires sensitive surface chemical methods, preferably with *in situ* examination. Techniques that have been applied include electron diffraction, ellipsometry, Auger, Mössbauer and Raman spectroscopy, XPS and EXAFS (see Chap. 7) (Sewell et al., 1961; Nagayama and Cohen, 1963; Foley et al., 1967; Seo et al., 1975; Sato et al., 1976; Tjong and Yeager, 1981; Löchel and Strehlow, 1983; Kruger, 1984; Hugot-LeGoff and Pallotta, 1985; Haupt and Strehlow, 1987; Meisel, 1989; Kamrath et al., 1990; Suzucki et al., 2001). Overall, the many different examinations by a variety of different methods have produced a reasonable consensus as to the composition of most types of rust and scale (Table 18.1). It should be noted here, that the conditions under which different Fe oxides form upon corrosion of iron, agree with what is found from laboratory synthesis experiments involving Fe^{II} and Fe^{III} salts (see Chapter 13). In other words, once the iron

Tab. 18.1 Composition of different rusts and scales on iron.

Type of corrosion	Conditions	Composition of the rust ^{a)}
Electrochemical	Stagnant pure water with enough O_2 ^{b)}	Gt, Lp
	Boiling water low in O_2 and/or acid ^{b)}	Mt
	Hot oxygenated water ^{b)}	Mt, Lp, GR
	Seawater	Mt, Lp, Gt, Ak
Atmospheric	Temperate and tropical environments	Lp, Gt (Mt)
	High SO_2	Gt predominates
	High Cl^-	Ak predominates
Passive layer	Anodic polarization in KOH/NaOH , H_2SO_4	Mt, Hm
	Borate buffer with Fe^{2+}	Lp
	Concentrated HNO_3	Spinel
Thermal	Air, room temperature	Mt, Mh
	Air, 250–550 °C	Mt, Hm
	Air, 600 °C	Wü, Mt, Hm

a) Gt: goethite; Lp: lepidocrocite; Ak: akaganéite; Hm: hematite; Mh: maghemite; Mt: magnetite; Wü: wüstite; GR: green rust; () trace

b) In pipes

metal has been oxidized, the oxides that are produced are the same as those that result, under the corresponding conditions, in the laboratory.

Oxide films can be stripped off iron by using bromine in methanol followed by heating at 300 °C in N₂ to remove FeBr₂ (Mayne and Ridgeway, 1971). The thickness of such films can be measured by weighing, by cathodic reduction and from the interference colours of the films; the latter technique can also be applied to measurement of film thickness *in situ*. The first order interference colours of hematite films on iron are yellow/brown, mauve, blue and silver grey and the second order colours are pinky-blue, blue and greenish-blue (Evans, 1963).

18.5.1

Iron oxides formed by electrochemical corrosion

In addition to iron salts, lepidocrocite, magnetite and goethite have been identified in rusts formed by atmospheric corrosion (Marti, 1963; Hiller, 1966; Keller, 1967, 1971; Misawa et al., 1974a; Schwitter, 1979; Oesch et al., 1994). Akaganéite has been found in rusts formed in the vicinity of high levels of chloride ions, for example, in marine environments and in chlorinated water (Sugawara et al., 1968; Keller, 1969; Bauer et al., 1986). It is also a significant corrosion product of Fe alloy phases on Antarctic meteorites where its formation is induced by the chloride ions coming from airborne seaspray and/or volcanic activity (Buchwald and Clarke, 1989). In these meteorites, akaganéite is located adjacent to the corroding surface and beneath a layer of goethite/spinel into which it eventually transforms.

Rust formed by atmospheric corrosion is often voluminous (Fig. 18.4) and visually appears as loose orange-brown or black masses. This type of rust is always a mixture of phases and frequently consists of two layers – magnetite at the iron/rust interface (as a result of reduced oxygen supply) with an outer layer of loose lepidocrocite and/or goethite. Hematite is formed during high temperature aqueous corrosion and is also found in the passive layer (which forms at room temperature).

Iron objects which are exposed to the atmosphere or are partly immersed in water are often subjected to alternate cycles of wetting and drying (Pourbaix, 1974; Schwitter and Böhni, 1980). These cycles may be due to seasonal fluctuations in weather conditions or be the result of tidal movements or of splashing. They cause the corro-

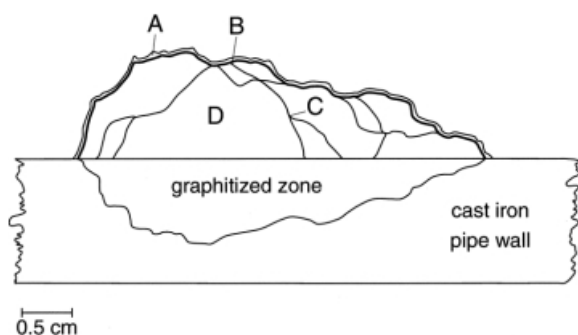


Fig. 18.4 Schematic representation of a cross section of a corrosion tubercle: A) Surface crust, B) magnetic membrane, C) internal chamber wall, D) fluid interior (Bigham and Tuovinen, 1985, with permission).

sion potential of the system to change periodically and this in turn, induces cyclic changes in the composition of the rust (Evans and Taylor, 1972). Such cycles have been simulated in the laboratory and studied using electrochemical and magnetic techniques combined with Mössbauer spectroscopy (Stratmann and Hoffmann, 1989; Marco et al., 1989). Stratmann and Hoffmann (1989) found that a dry, corroded iron surface had a corrosion potential of ca. +0.2 V which upon wetting, gradually shifted to -0.4 V owing to retarded diffusion of oxygen from the air to the metal. The reactive component of the rust, lepidocrocite, was thus reduced via an intermediate (probably green rust) to magnetite with simultaneous corrosion of the metal. During the drying cycle, the oxygen diffused back through the pores in the oxide layer and the magnetite was oxidized to maghemite. If, however, reduction went only as far as the intermediate state, this phase was oxidized to lepidocrocite. During the wetting/drying cycles, the morphology of the oxide particles changed and this broke up the rust and prevented its adhesion to the underlying metal. At potentials lower than -0.5 V, any goethite in the rust was partly reduced, but usually, the potential drop in the wetting/drying cycles was only sufficient to reduce the thermodynamically less stable Fe^{III} oxides.

A feature of rust, particularly of magnetite (which is an electronic conductor) is its ability to reduce oxygen to a far greater extent than does the metal (Evans and Taylor, 1972). Thus, once some rust has formed, corrosion may be accelerated. This is also one reason why, if all rust is not removed from a metal surface before application of a protective paint coating, corrosion continues under the film. Similarly, akaganéite residues on meteorites promote corrosion under the conditions of ambient humidity and this leads to disintegration of such meteorites in museums (Buchwald and Clarke, 1989).

Sulphur dioxide, a widespread atmospheric pollutant, generally accelerates corrosion of iron and steel (Schikorr, 1967; Evans, 1968); it is oxidized to sulphuric acid which reacts with the iron to form Fe^{II} sulphate. Schwarz (1965) reported that in the early stages of the rusting process, Fe^{II} sulphate was located in the inner part of the rust close to the metal and was gradually oxidized to a thin crust of goethite and lepidocrocite at the surface of the rust. Other workers also noted that the level of sulphur species decreased with time, but considered that the sulphate was concentrated in the outer layers of the rust (Gancedo et al., 1988; Davalos et al., 1991). Goethite, lepidocrocite and magnetite were found in rust formed in the presence of SO_2 containing environments in Sweden (Singh et al., 1985). The goethite-to-lepidocrocite ratio increased as the level of atmospheric SO_2 rose. It was suggested that sulphate species accelerated the conversion of lepidocrocite to goethite, although it is equally likely that the two phases formed competitively, with goethite being promoted by sulphate species.

Rusting (or scaling) can be a problem in water pipes. In pure water, iron corrodes to a voluminous, poorly ordered Fe^{III} oxide (probably ferrihydrite), but if the oxygen supply is limited, a non continuous deposit of magnetite forms. In the boilers of central heating systems, a protective film of magnetite lines the pipes after some months, provided that air and acid are excluded. Where oxygen leaks occur (often in poorly designed systems), some lepidocrocite and/or green rust may be found as

well. Frequently there is also an admixture of calcite or aragonite, siderite and even traces of iron sulphide, all of which enhance the thickness of the scale (Hiller, 1966; Feigenbaum et al., 1978; Sontheimer et al., 1981). The composition, structure and protective character of pipe and boiler scales depend upon such factors as flow rate of water, the level of dissolved oxygen, the water chemistry and temperature and the length of the corrosion period (Bengough et al., 1931; Butler and Stroud, 1965; Butler and Benyon, 1967). In a combined bacterial, chemical and mineralogical study of rust tubercles formed in drinking water pipes, an array of Fe oxides was identified (Fig. 18.4) (Tuovinen et al., 1980; Bigham and Tuovinen, 1985). The anoxic interior of the tubercles consisted of green rust forming hexagonal plates (Fig. 18.4D, Fig. 18.5), overlain by magnetite (Fig. 18.4B), with goethite and lepidocrocite at the outer surface of the tubercle (Fig. 18.4A). The magnetite probably formed by oxidation of the green rust. In the interior of the older tubercles, magnetite was oxidized to maghemite. The carbonate form of green rust was also identified in the inner layers of rust tubercles in pipes for drinking water (Stampfl, 1969).

Refait et al. (1998) showed with Mossbauer spectroscopy that $\text{Fe}(\text{OH})_2$ formed on Fe coupons held (at room temperature) in KCl (pH 9) solution at a potential of -0.55 V, whereas at -0.35 V, the main corrosion product was green rust.

Information about the corrosion of boiler piles comes from analysis of scale samples and also from laboratory experiments. Smith and McEaney (1979) used XRD and SEM to follow the initial stages in the development of scale on gray, cast iron in water at 50°C . At first, the corrosion product was a mixture of magnetite and green rust. Whether lepidocrocite formed depended on the level of oxygen in the system,

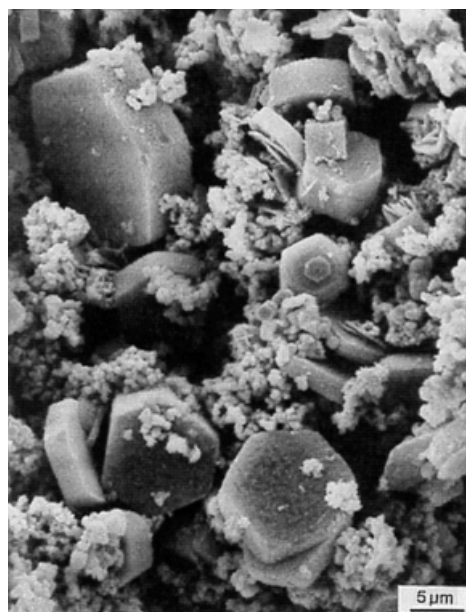


Fig. 18.5 Scanning electron micrograph of a tubercle from a corroded water pipe showing large hexagonal plates or prisms of green rust and small Fe^{III} oxide crystals, probably lepidocrocite and goethite formed from oxidation of green rust (Bigham and Tuovinen, 1985, with permission, courtesy J. M. Bigham).

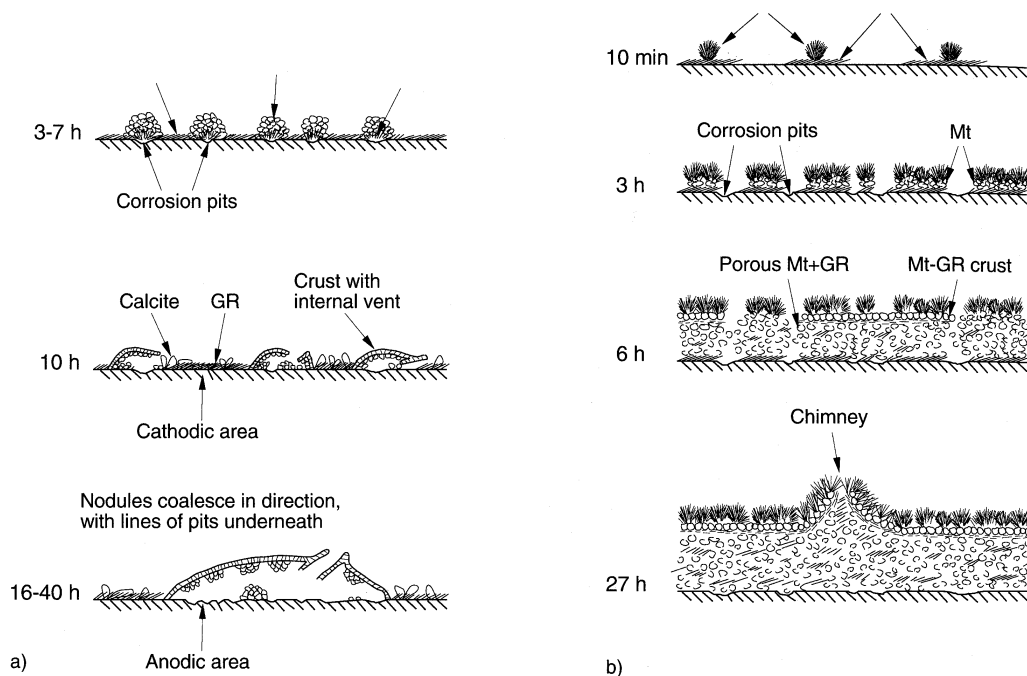


Fig. 18.6 a) Stages in the development of scale on grey cast iron in water at 50 °C with 0.44 mg L⁻¹ O₂; b) Stages in the development of scale on grey cast iron in water at 50 °C with 3 mg L⁻¹ O₂ (Mt: magnetite, GR: green rust) (Smith and McEaney, 1979; with permission).

i.e. on the rate of oxidation (Kassim et al., 1982). With low levels of oxygen (<1 mg L⁻¹), the rust tubercles (or nodules, as they are sometimes termed), coalesced to form a more or less continuous film and a crust of magnetite formed over the porous component which gradually dissolved (Fig. 18.6a). In addition, the aragonite form of calcium carbonate precipitated between the nodules. In the presence of higher levels (>3 mg L⁻¹) of oxygen, laths of lepidocrocite grew out of the surface of the green rust deposits (Fig. 18.6b). After some hours, the scale consisted of a mixture of large plates of green rust and small particles of magnetite, all overlain by needles of lepidocrocite. The scale gradually became continuous and again a crust formed over the porous material. With time, the magnetite component increased at the expense of the green rust and lepidocrocite (Fig. 18.7), which accords with field observations that the scale from boiler pipes consists solely of magnetite. Smith and McEaney (1979) considered that magnetite and green rust precipitated independently. Although this is feasible, other SEM studies have shown growth of magnetite on large, hexagonal crystals of green rust (McGill et al., 1976). After ca. 27 h, "chimney-like" vents appeared in the scale through which presumably gaseous corrosion products escape.

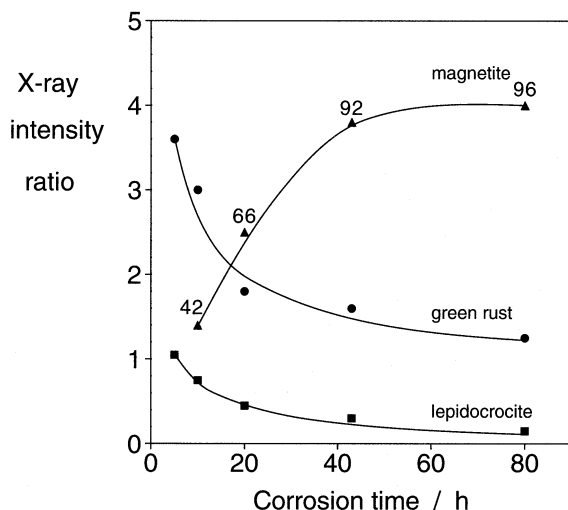


Fig. 18.7 Changes with time in the levels of the three iron oxide components of scale on grey cast iron (Smith and McEaney, 1979, with permission).

Pipes through which high temperature ($\geq 100^\circ\text{C}$) water flows may be lined with a duplex film consisting of an inner layer of magnetite and an outer layer of hematite. The inner surfaces of the cooling coils in nuclear power plants are coated with magnetite (Lipka et al., 1990) and considerable work has been directed to developing suitable (complexing) dissolution agents to assist in the removal of these deposits (Regazzoni et al., 1981; Ardizzone et al., 1983; see also Chap. 12). The difficulties of cleaning these pipes are increased by the incorporation of small amounts of radioactive cobalt in the magnetite to form a radioactive scale (Music and Ristic, 1988).

Buried iron/steel objects also corrode (Plate 18.1). The corrosion scale on mild steel plates which had been buried in a range of New Zealand soils for 24 years consisted predominately of 10 nm particles of (superparamagnetic) goethite together with small amounts of akaganéite, lepidocrocite and magnetite (Johnston, 1978). The rust of the mousetrap in Plate 18.1 consisted of goethite and maghemite. Rust found on an ancient, buried iron axe head from India consisted of very poorly crystalline lepidocrocite (Raman et al., 1991). Odziemkowski et al. (1998) showed with normal and surface enhanced Raman spectroscopy, that $\text{Fe}(\text{OH})_2$ was the precursor of magnetite that formed on iron during anaerobic corrosion. A duplex magnetite/hematite layer formed around a steel bar that had corroded in concrete; the pH at the interface was ca. 12.6. The oxide layer had a thickness of up to 1.5 mm (Gallias, 1999; Aligizaki et al., 2000).

18.5.2

Iron oxides in passive films

Passive layers on iron are often only a few molecular layers thick and hence, are optically invisible. They are protective because they are nonporous, uniform and adhere firmly to the metal. There is still some uncertainty about the composition of the pas-

sive film due both to the difficulty of analysis of such thin films and because their composition may vary with the polarization potential and the nature of the electrolyte (Thomas and Davis, 1977). Some authors have suggested that the passive film formed on steel at fairly positive potentials is “hematite-like” and that formed at more negative potentials is “magnetite-like” (Sato et al., 1976). In general, however, the data from a range of techniques are considered to indicate a two layer film (“sandwich model”) with an Fe^{II} oxide adjacent to the metal and an Fe^{III} oxide making up the outer layer.

Raman spectroscopy showed the presence of maghemite as well as salts in the passive film formed upon immersion in a concentrated solution of HNO_3 (Hugot-LeGoff, pers. comm.). Electron diffraction studies and *in situ* Raman spectroscopy applied to passive films formed by polarization of iron in M KOH, 0.5 M H_2SO_4 and also in borate buffer (pH 8.4) indicated that the film had an inner layer of magnetite and an outer layer of hematite under all the above conditions¹⁾ (Sewell et al., 1961; Froelicher et al., 1983). A combined Mössbauer, Auger and XPS study suggested that the oxide layer on steel passivated in Na_2SO_4 or $\text{NaH}_2\text{PO}_4\text{-H}_3\text{PO}_4$ solution, consisted of three layers – an inner one of Fe_{1-x}O , an intermediate layer and an outer layer of FeOOH or hematite. The intermediate layer, which was only a few molecular layers thick and highly disordered, was considered to be the actual protective layer (Meisel, 1989). The same study showed that the passive layer formed on stainless steel (X1Cr Ni Si 1815), upon boiling in HNO_3 , consisted of SiO_2 with no trace of Fe oxide. A potential-modulated reflectance spectroscopy study appeared to indicate that the passive film consisted of an Fe^{II} compound (at all potentials) together with a layer of FeOOH that was increasingly replaced by Fe_2O_3 upon increasing the anodic potential (Larramona and Gutiérrez, 1989). Raman spectroscopy data suggested that in the very earliest stages of passivation, an amorphous layer formed and gradually recrystallized (Hugot-LeGoff and Pallotta, 1985). Passive films formed in phosphate buffer were initially a mixture of hematite and Fe^{III} phosphate which later converted to hematite. It is probable that the discrepancies between the various studies arise, at least in part from differences in interpretation of the various spectroscopic measurements. The passive film loses its stability when the applied potential is removed; i.e. it dissolves thus enabling corrosion to proceed unhindered. The very rapid dissolution of the passive film involves a reductive mechanism, not proton attack (Pryor and Evans, 1950).

18.5.3

Thermally grown oxide films

The oxide film formed in dry air at room temperature consists of a spinel phase, probably a solid solution of magnetite and maghemite. Such films form on magnetic tapes. They are around 1.5–2.0 nm thick, and in a dry atmosphere, can provide indefinite protection (e.g. the Delhi pillar). Ali and Wood (1969) found that with time and at a relative humidity of 46%, some hematite developed as well. At higher temperatures (200–300 °C) well defined duplex films with an inner layer of magnetite

1) Note that these passive layers which contained hematite were formed at room temperature.

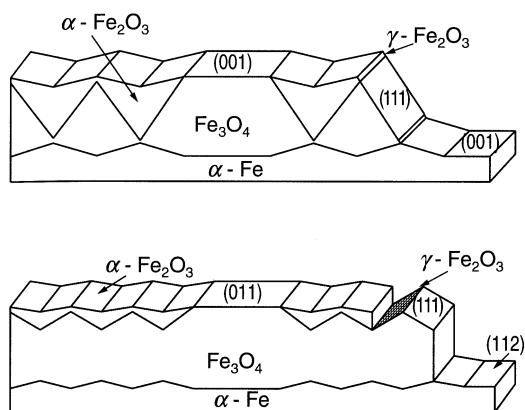


Fig. 18.8 Proposed structures of the oxide film formed on iron at 350 °C (Seo et al., 1975, modified, with permission).

and an outer layer of hematite formed (Seo et al., 1975). The interface between the two layers was irregular.

The rates of oxidation of different planes of a single crystal of α -Fe were followed over the temperature range 250–550 °C by observing the different interference colours of the oxide film at different times, and the composition of the films found using glancing X-ray diffraction (Wagner et al., 1961). The interference colours vary with film thickness. The rate of oxidation for the different planes of α -Fe decreased in the order; (001) > (111) > (011) > (320). At 250 °C and low pressures of oxygen, the scale on all four planes consisted of magnetite. With thin films, epitaxy is important; the orientation of these films depended on the plane of α -iron on which growth had taken place. The predominant orientation was (001) Fe_3O_4 // (001) α -Fe with the [110] axis of the magnetite parallel to the [010] axis of the iron (Fig. 18.8). The situation reflects the optimum match between the two structures. Different epitaxial relationships are observed on the other iron planes (Tab. 18.2). At higher temperatures (550 °C) and oxygen pressures, the scale consisted of an inner layer of magnetite and an outer layer of hematite.

Tab. 18.2 Orientation relationships between iron and iron oxides.

<i>Iron plane/direction</i>	<i>Oxide</i>	<i>Oxide plane/direction</i>
(111)	Hematite	(211)
(001)	Hematite	(114)
(001) // [010]	Magnetite	(001) // [110]
(111) // [011]	Magnetite	(210) // [100]
(011) { [100]	Magnetite	(111) // [101] or [110]
(001)	Maghemite	(001)
(001)	Wüstite	(001)

Epitaxial planes in scale:

(001) α -Fe // (001) FeO // (001) Fe_3O_4

(011) α -Fe // (111) Fe_3O_4 // (001) α - Fe_2O_3

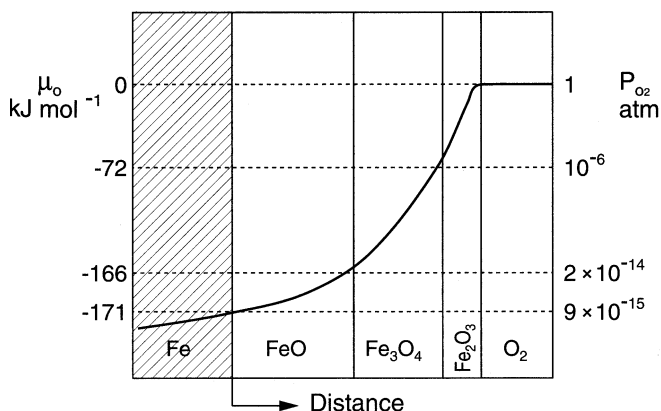


Fig. 18.9 Oxygen potential gradient through the complex scale formed on iron at 1000 °C (West, 1980, with permission).

The oxide scale formed on iron and steel at temperatures above 600 °C consisted of wüstite, magnetite and hematite. A complex oxide film forms because the different oxides are stable at different oxygen partial pressures and both the oxygen concentration and the equilibrium potential vary across the film. Figure 18.9 illustrates the change in composition with varying oxygen partial pressure for a scale formed on iron at 1000 °C. This type of scale forms on steel emerging from a rolling mill (millscale). If the scale is cooled slowly, the wüstite decomposes to magnetite and iron. Millscale must be removed before the steel is coated with a nonferrous metal and this is achieved by pickling, i.e. immersion of the steel in warm, dilute sulphuric acid or cold HCl; the scale dissolves reductively. The pickling acid/Fe solution is used as a raw material in the pigment industry (see Chap. 20).

Burnishing is the formation of black-brown oxide films on iron and its alloys by controlled oxidation of cleaned metal surfaces. These films are extremely complex and contain, in addition to maghemite and magnetite (or a substituted magnetite for Ni, Mo or Co alloys), various nitride phases – Fe_4N , Fe_3N and FeN . The nitride phases are adjacent to the metal and the iron oxides are in the outer layers of the film (Gebhardt, 1973).

18.6

Prevention of corrosion; protective oxide layers

The enormous cost of corrosion of iron to society has prompted many efforts to devise ways of reducing or preventing it. Several electrochemical or chemical methods are available. One method is removal of the cathodic species (usually oxygen). Most methods are based on the principle of providing a barrier between the reacting species. The barrier may be *physical*, i.e. a metal or paint coating or a protective oxide film, or *electronic*, i.e. making the iron thermodynamically immune. Here, the em-

phasis is on the protective film. It must be uniform, nonporous and adherent. Such films do not form during atmospheric rusting (Hiller, 1966). Examples of protective films are the passive film that forms upon contact of iron with concentrated nitric acid on iron or at low temperature in an unpolluted atmosphere and the rust that forms on antiweathering steels. Formation of these protective films is often achieved either by addition of inhibitors to water in contact with iron (e.g. in water pipes) or by alloying iron with low levels of other elements. Such methods reduce corrosion, rather than prevent it. The metal slowly rusts, sometimes for two or three years, until a stable film which significantly slows further rusting, has formed.

Inhibitors modify the corrosion process and alter the products. Anodic inhibitors deactivate the anodic sites on the metal and by raising the corrosion current above the current density necessary for the onset of passivity, bring the potential into the passive region of the Pourbaix diagram. Such inhibitors are the nitrite and chromate ions. Nitrite is a powerful enough oxidizing agent to ensure that the corrosion products are all in the trivalent state and in its presence, an Fe^{III} oxide film forms very rapidly. Chromate, which is another strong oxidizing agent, interacts with the iron and induces formation of a continuous, mixed precipitate of Cr_2O_3 and Fe_2O_3 . The presence of these inhibitors can also assist in repairing oxide films by promoting rapid formation of new oxide deposits to plug holes in the film. When using such inhibitors, it is essential that their concentration is high enough to bring the iron into the passive region; if the concentration is lower than this, iron is still in the corrosion domain and corrosion is actually enhanced.

Cathodic inhibitors promote coverage of iron by a protective coating, but this need not be an iron oxide. Immersion of iron in a solution of phosphoric acid containing a suitable catalyst causes precipitation of a mixed $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ phosphate film which serves as a base for a coating of paint.

Alloying iron with nickel or with at least 120 g kg^{-1} of chromium ensures that the metal is passivated by milder oxidants than is the case for pure iron. Alloying can also raise the driving emf required for corrosion to take place. The high corrosion resistance of alloyed steels is attributed to the enrichment of chromium in the protective film; the film that forms on austenitic steels ($10 \text{ g kg}^{-1} \text{ Cr}$, $80 \text{ g kg}^{-1} \text{ Ni}$) consists mainly of Cr_2O_3 with varying admixtures of the other elements in the steel including Fe and Ni (Asami et al., 1978). Alloying also reduces the rate of high temperature oxidation of steel. On an Fe-Cr alloy, the inner layer of scale consists of an Fe-Cr spinel and the outer layer of hematite.

Antiweathering steels contain at most, a few tens g kg^{-1} of copper, chromium or phosphorous (Evans, 1968; Misawa et al., 1971). These additives modify the rust so that it grows slowly, over some years, to a protective film. The inner part of such films is reported to be coherent and to adhere to the metal, whereas the outer part is loose; the particles of oxide in this type of film are smaller than those found in rust grown on unalloyed iron (Davalos et al., 1991). Haces et al. (1991) reported that rust formed on alloyed steels during atmospheric corrosion tests over a three year period, consisted of a mixture of goethite and lepidocrocite; there was some gradual conversion of lepidocrocite into goethite. Initially, all three steels corroded at the same rate, but after ca. 12 months, the rate for the Cu-steel ($3 \text{ g kg}^{-1} \text{ Cu}$) decreased far more ra-

pidly than did that for the Ni or Cr steels, suggesting that a protective film had formed more rapidly on the Cu steel. Imaging atom probe analysis combined with electron diffraction, showed that rust formed (at room temperature) within hours on a steel wire containing 9 g kg^{-1} Cu and consisted of a mixture of a spinel phase and electron amorphous Fe^{III} oxide hydroxide (Cornell et al., 1989c). The rust was enriched in copper (ca. 10 fold more than in the metal) and it was suggested that Cu was present in the spinel structure. Rust formed on weathering steels exposed to the atmosphere for 11 years in the USA consisted of a dark, porous, inner layer which Raman spectroscopy showed to consist of goethite and lepidocrocite overlain by a smooth, outer layer consisting of magnetite (Townsend et al., 1994).

The stability of antiweathering steels appears to be extremely dependent upon variations in the levels of pollutants in the atmosphere. COR-TEN (an antiweathering steel containing Cu, Cr and Ni) was used successfully in the 1960s on buildings in North America; once the protective rust had formed further corrosion appeared to be halted (Evans, 1968). In Europe, on the other hand, structures built of this material have corroded significantly after 15–20 years; this may reflect increasing atmospheric pollution. The main component of the rust formed on such steel was lepidocrocite together with a small amount of goethite and some copper hydrosulphate (R. Giovanoli, pers. comm.).

Anticorrosive paints containing pigments with either chemical or electrochemical action may induce formation of protective coatings at the metal-paint interlayer (Etzrodt, 1993). These protective coating may be metal-substituted iron oxides iron phosphate precipitates or even a green rust – $\text{Fe}_6^{\text{II}}\text{Fe}_2^{\text{III}}\text{OH}_{18}\text{CO}_3 \cdot 4 \text{H}_2\text{O}$ (Chemical Week, 1988).

19

Applications

19.1

Historical background

For thousands of years, iron oxides have been used as colouring agents. Prehistoric man took advantage of the light fast yellow and reds that could be obtained from local deposits of (so-called) ochre to produce cave and rock paintings. These testimonies of age-old cultures have been found in astonishingly diverse regions; everywhere in fact where suitable, ochre deposits were available – the Sahara region, central Australia, South Africa, Southern France, Northern Spain, along the old silk road and in many more areas. The modern tourist industry of such regions has profited from the fortuitous deposits of iron oxides. Nowadays, thousands of people come each year to admire and marvel at the cave paintings at Lascaux and Altamira and the rock art of the Australian aborigines and the bushmen of South Africa. So many tourists came to Lascaux that the caves were recently closed to the public to protect the paintings from decay; a full-size copy of the hall of bulls has, therefore, been produced.

As man progressed and technology developed, the applications of iron oxides as colorants were extended. By around 2000 BC, the practice of calcining raw ochres to produce a range of reds and browns was well established; it may have been developed centuries earlier. Pomies et al. (1999) examined upper Palaeolithic (ca. 10,000 BC) rock paintings at an archaeological site in the French Pyrenees and found that the hematite used there had been obtained by heating goethite; the crystals were porous which indicates a dehydroxylation process had occurred (cf. Chap. 14). From around the fifth or sixth millennium BC, raw ochres were also reduced to a black pigment by briefly heating vessels to which a layer of ochre had been applied, at 800 °C in a sealed kiln. This iron reduction technique was particularly important in Mesopotamia and Minoan Crete (Noll, 1979, 1980). In antiquity, raw and calcined ochres provided colours for the decoration of ceramics, pottery and wall murals. The famous red and black vases of ancient Athens owed their colours to hematite and magnetite (Hofmann, 1962; Lagaly, 1984). They formed a vital export item, the currency from which helped to pay for the importing of essential grain supplies. Hematite was also the source of the bright red colour of the funeral vessels used in France and Southern England in the late Bronze/early Iron age period. An

excellent example of this is the Prunay vase (4th century BC, now in the British Museum) (Rigby et al., 1989). Red, Samian table ware was mass-produced by the Romans in Southern France. Before firing, a layer of fine clay (slip) containing hematite and a high level of illitic clay, was applied to the surface of the pottery. The hematite provided the red colour and the parallel alignment of the illite plates was responsible for the high quality, glossy finish of this ware (Middleton, 1987, 1992). Interestingly enough, a similar technique has been used to produce present day interference pigments (see section 19.2.2).

Iron oxides, themselves, were valued commodities. One high quality hematite used to be shipped from the Black Sea port of Sinope to Minoan Crete and Egypt where it was used as a pigment for wall paintings. The pigment was called sinopia and centuries later, the name persists in French; *la sinopie* is the synonym for the rough drawing for a wall painting.

Another early use of iron oxides was as a cosmetic. The cosmetic boxes (cockle-shells) found in the “Royal Cemetery” in the ancient Sumerian city of Ur contained a range of different colours. XRD analysis by the Research Department of the British Museum showed that the principal components of the red and yellow colours were hematite and goethite, respectively (Bimson, 1980). One box also contained a purple powder consisting of a mixture of quartz grains and large crystals of hematite.

Iron oxides have never lost their importance in art and decoration (Plate 19.1). Mediaeval and later artists used them in frescos and other paintings. Sometimes, unusual effects were obtained by mixing the iron oxide with another inorganic pigment. For example, flesh-coloured tints could be obtained using a mixture of ochre and cinnabar. Over the centuries more and more uses of iron oxides as pigments have been developed; these often involve varied and unusual effects. The metallic paints used on automobiles and the colours of certain pharmaceutical products as well as the more traditional red brick houses in parts of England, pink paving stones in shopping malls and red-floored tennis courts, provide examples of modern applications of these pigments.

Centuries after man had started to use iron oxides as colouring agents, he discovered how to smelt them. The first iron was produced between 4000 and 2000 BC. Since then, this product of iron oxides has been used in weapons, utensils, tools, implements and construction. The extensive English iron ore deposits contributed to the lead England acquired in the Industrial Revolution.

Iron oxides have played their part in navigation. Around the first millenium AD, magnetite, in the form of lodestone, was used in the earliest, crude mariners compasses. These enabled more difficult voyages to be undertaken and thus contributed to a furthering of trade and exploration.

The most important modern applications of iron oxides are as ores for the iron and steel industry and as pigments (Heine and Volz, 1993). Fe oxides are also used extensively as magnetic pigments in electronic recording devices and as catalysts in industrially important syntheses. Other minor, but still important applications are listed in Table 19.1 and are discussed in the following sections.

Tab. 19.1 Applications of iron oxides.

Pigments for paints and the construction industry ^{a)}
Magnetic pigments and ferrites ^{a)}
Catalysts for industrial syntheses ^{a)}
Raw materials for the iron and steel industry ^{a)}
Adsorbents for water and gas purification and for low level radioactive waste decontamination
Ferrofluids
Jewellery (hematite)
Laboratory and industrial chemicals
In production of photochemicals
In oil well drilling muds as weighting agents
In animal feeds
In production of fertilizers
In soil amelioration (e.g. red mud)
In removal of sulphur from coal gas
In nonferrous smelting industries
In mineral separations (e.g. coal-washing)
In battery and welding electrodes
In air bags in automobiles
In medicine
In cathode ray tubes
In flame retardants
For polishing optical lenses

a) Major applications

19.2

Pigments

As pigments, iron oxides have a number of desirable attributes. They display a range of colours with pure hues and high tinting strength. They are extremely stable, i.e. non-bleeding, non-fading and highly resistant to acids and alkalis and can, therefore, be exposed to outdoor conditions (Winter, 1979). The red wooden houses which are such a feature of the Swedish landscape and the buff- and ochre-coloured buildings throughout the world (Plates 19.IIa and b, see p. XXXV), for example, owe their colours to iron oxide based paints; the hematite used on the Swedish houses actually comes from roasting pyrites. The yellow pigments are thermally stable to ca. 180 °C and the reds are heat resistant to 1200 °C (in oxidizing conditions). The pigments can be used in both water- and organic-based paints. Iron oxides are strong ultraviolet (UV) absorbers and hence, protect the binder in the paint from degradation. As iron oxides are nontoxic and, as the synthetic ones are completely free from crystalline SiO₂, they can be used as colouring agents in food and in some pharmaceuticals. A further advantage is that iron oxides can be produced at low cost.

Until the beginning of this century, the needs of the pigment industry were supplied by natural iron oxides. Pigments produced from ochres in Southern France

were exported world wide by firms such as Lamy.¹⁾ In addition to their other properties, the small particle size and comparatively narrow size distribution of the ochres made them particularly suitable for use as pigment (unlike various other coloured minerals).

Since then, these materials have been increasingly supplanted by their synthetic analogues. The latter can be produced in very pure form with extremely consistent properties. Today, natural iron oxide pigments account for only around 20% of world consumption. The main producers of natural iron oxide pigments are France, India, Cyprus, Iran, Italy and Australia (Buxbaum & Printzen, 1993).

19.2.1

Natural pigments (Plate 19.III, 19.IV, p. XXXVI–XXXVIII)

The natural iron oxide pigments are termed the *ochres*²⁾ which are yellow and contain goethite (10–50%) as the Fe oxide constituent, the *reds*, with a high content of hematite, the medium to dark yellow *siennas*, the *umbers* and the *blacks*, which consist of magnetite (Benbow, 1989; Buxbaum & Printzen, 1993).

The different names of the reds – Spanish red, Persian red and Winford red (UK) – reflect some of the sources of these pigments. The characteristic greenish-brown or grey colour of the umbers comes from the presence of organic matter and 5–20% MnO₂, as well as the iron oxide, in this pigment. Calcination of the siennas and the umbers produces *burnt sienna* (red/orange) and *burnt umber* (deep brown), respectively. Cyprus and the USA are the main sources of the siennas and the umbers. The *metallic browns*, red to dark purple pigments containing large crystals of hematite, are obtained by calcination of siderite (FeCO₃) or the yellow ochres; these pigments are important in the USA. An important natural hematite is *micaceous iron oxide* (MIO). Natural *magnetite* has a low tinting strength and its use as a pigment is declining. *Van Dyke Brown* (from Germany) is not regarded as being a true iron oxide pigment because, despite its iron oxide content, it has a very high level of organic matter. The green earth *terre verte* (from Italy) contains Mn₂O₃ and complex silicates as well as iron oxide. Both the latter pigments are used in artists' colours.

Natural pigments are often intermixed with clays and SiO₂ and, in some cases, with organic matter and/or MnO₂. High levels of MnO₂ are undesirable in pigments because this mineral can cause paint to dry too fast and also induces brittleness in rubber. The iron oxide content of unrefined, natural pigments (expressed as % Fe₂O₃) is variable being least for the yellow ochres (10–50% Fe₂O₃) and highest for the reds for which it may exceed 90% Fe₂O₃.

Considerable effort is needed to transform natural ochres into commercially acceptable pigments (Bec, 1986). In Southern France, for example, the ochre is mined using mechanical shovels and then washed, decanted, dried and ground. This extracted material is separated from the associated clay and sand with an electric cen-

1) Lamy went out of business in the early 1990s.

2) Ochra (latin) from ochros (greek) = pale yellow, although there are also red ochres. In the 3rd millenium BC, the dead, in some societies,

were painted with red ochre because red was considered to be the colour of life (Wilke, 1927).

trifuge; the washed ochre must contain less than 1.5% of these impurities. The ochreous slurry is then allowed to settle in large, open air pits, evaporated over some months and dug out as bricks which are allowed to dry out in air. In the factory, these bricks are crushed and then micronised. By careful blending of the different samples of ochre, a great variety of extremely reproducible shades of red, yellow and brown can be produced.

Natural iron oxides are used, like their synthetic counterparts, predominantly in the construction and coating industries (Kendal, 1994). The emphasis, particularly in recent years, has been on colouring concrete bricks and paving stones. Iron oxides are among the few pigments approved by the ASTM (American Society for Testing and Materials) for use in highly alkaline environments. Up to 10% pigment may be incorporated in the concrete; higher levels can influence settling time and reduce compressive strength. The pigments are also used in clay bricks, in roof tiles and in mortar which is coloured to tone in with or match the bricks. Red iron oxide, particularly red, Spanish oxide and the Winford red from the U.K. is used extensively for such purposes. The Spanish oxide is also used in Spain for the production of red floor and wall tiles (Regueiro et al., 1997).

A further important application of these pigments is in paints. The natural red iron oxides are also used in primers for steel structures and cars, for marine coatings and for anti-fouling paints. In the USA, the metallic browns are used for these purposes. The level of soluble salts in the latter pigments is low and this reduces corrosion problems. The metallic browns are also used in heat resistant enamels.

The umbers were used formerly to colour bakelite. Nowadays they are used in enamel coatings for which their small particle size ($< 20 \mu\text{m}$) makes them very suitable. Further application of iron oxide are in woodstains, papers (including cigarette papers and cardboard), for colouring rubber, as frits and glazes for ceramics and for tinting glass. Iron oxides also colour plastics, for example, red and yellow rubbish bags. The siennas and ochres are used in crayons, chalks and artists colours. Iron oxides are added to animal feedstuffs both for colour and as an iron supplement. In the USA, natural magnetite finds application in ceramic magnets, brake linings, agricultural supplements, bricks and in magnetic inks for laser printers, fax machines and photocopiers.

Micaceous iron oxide (MIO) is a specialty pigment which is used world wide in heavy duty, anticorrosion paints for steel structures – bridges, industrial plant, pylons, storage tanks and off shore oil rigs (Benbow, 1989). Every railway bridge in England has a top coat of paint based on MIO as does the Eiffel Tower in Paris. Micaceous iron oxide has a sparkling grey to black appearance and consists of large lamellar plates of specular hematite, 1–100 μm across and ca. 5 μm thick.

The level of insoluble salts associated with this pigment is very low. In the paint, the pigment particles pack together to form an overlapping array of parallel platelets which hinder the movement of inorganic ions and provide a barrier to penetration of the paint film by water and oxygen. It is, therefore, the lamellar habit of the particles which is responsible for the anticorrosion properties of this pigment. In addition, the pigment absorbs ultraviolet radiation and so protects the binder against degradation. MIO is chemically inert, so the protection it provides is simply physical. As

MIO is nontoxic, it is more environmentally acceptable than the lead and chromate based paints which are used to provide chemical protection in other anticorrosion paints and primers (Etzrodt, 1933). The highest quality (with respect to the flatness of the particles, aspect ratio, etc.) MIO comes from the mine at Waldenstein in Austria (Producer; Kärntner Montanindustrie), but there are also mines in Spain, South Africa and Western Australia. The supply of highest quality MIO, which used to be mined in Devon in England, was exhausted during the 1970s. This was one of the factors which prompted the U.K. workers to seek a method of making synthetic MIO (Carter, 1988; see Chapter 20).

19.2.2

Synthetic pigments

The first synthetic iron oxide pigment, Venetian Red, was produced towards the end of the last century by calcining a mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (copperas) and lime. This was followed and overtaken by Copperas Red formed by calcination of copperas alone. Since that time, the synthetic pigment industry has developed enormously and the annual world production of synthetic iron oxides is currently ca. $\leq 600,000$ t. The major producers are Germany, USA, U.K., Italy, Brazil and Japan with more than 50% of all synthetic iron oxides coming from Germany. Australia and Sweden are minor producers. The two companies with the greatest output of iron oxides are Bayer (Germany, trade name of product BAYFERROX and Harcross (U.K./U.S.A.)). Other important manufacturers include BASF and Merck (Germany), Toda (Japan), Oxhisa (Spain), Miles (U.S.A.). BAYFERROX is produced in over 300 different shades of yellow, red, brown and black.

The major synthetic iron oxide pigments are the yellows (goethite), the oranges (lepidocrocite), the reds (hematite), the browns (maghemite) and the blacks (magnetite) and mixtures of these (Tab. 19.2) (Buxbaum & Printzen, 1993). Akaganéite is not used as a pigment. Production of the synthetic iron oxides involves three basic methods; precipitation from soluble Fe^{II} salts by a hydrolysis/oxidation process, solid state transformations and reduction of nitrobenzene using scrap iron. These processes are described in Chapter 20. The iron oxide crystals are produced in a variety of shapes – spherical, acicular, rhombohedral and cubic. By modifying the shapes and sizes of the particles, a variety of shades may be produced (see Chap. 6).

Like the natural iron oxide pigments, the synthetics are used for colouring concrete, bitumen, asphalt, tiles, bricks, ceramics and glass. They are also used extensively in house and marine paints. Because the shapes of the particles can be accurately controlled and the particle size distribution is narrow, synthetic iron oxides have a greater tinting strength than the natural ones and so, are chosen where paint colour is important, i.e., for top coats. Red iron oxides are used in primers for automobiles and steel structures.

Other uses of iron oxide pigments are in porcelaine, rubber, paper, in floor and furniture stains, plastics, fabrics and in leather finishes. Iron oxides are especially suitable colourants for floor coverings as their resistance to alkali enables them to

Tab. 19.2 Synthetic iron oxide pigments.

<i>Type</i>	<i>Formula/Mineral Name</i>	
Yellow	α -FeOOH/Goethite	96–97 wt% FeOOH
Orange	γ -FeOOH/Lepidocrocite	
Red	α -Fe ₂ O ₃ /Hematite	92–96 wt% Fe ₂ O ₃
Brown	γ -Fe ₂ O ₃ /Maghemite	
Black	Fe ₃ O ₄ /Magnetite	92–96 wt% Fe ₂ O ₃
Anticorrosive	Micaceous iron oxide (α -Fe ₂ O ₃)	
Mixed anticorrosive	ZnFe ₂ O ₄ /Zinc Ferrite	
Mixed	(Fe,Mn) ₂ O ₃ -bixbyite structure, black (Fe,Mn) ₂ O ₃ -corundum structure, brown	
Interference	Hematite particles on mica	
Transparent	α -FeOOH and α -Fe ₂ O ₃ (50–100 nm)	
Magnetic	γ -Fe ₂ O ₃ /Maghemite	99.5–99.8 wt% Fe ₂ O ₃
	Fe ₃ O ₄ /Magnetite	

withstand strongly alkaline cleaning compounds. They also colour food, for example, cheese rinds, pet foods, fish pastes and sweet decorations (Watson, 1979) and cosmetics such as powders, rouges, lipsticks and nail varnishes. Face powder with practically any skin tone can be produced by using appropriate combinations of yellow, red and black iron oxides (Love, 1998). Iron oxides can also protect pharmaceutical products against the degradative effects of UV light and may be used to colour the capsules of various pills.

Besides the major iron oxide pigments, there are the specialty pigments. These are the transparent reds and yellows, the synthetic MIO's, the interference pigments, the mixed iron oxides and the magnetic pigments. The transparent yellows consist of acicular crystals of goethite between 50–100 nm in length (Gaedcke, 1993). They can be transformed into the transparent reds (hematites) of the same size and shape by calcination at 400–500 °C. Blending of the reds and yellows gives a variety of transparent shades. The coloured pigment particles become transparent in the binder if the particle size is small enough and in addition, the difference between the refractive index of the pigment and that of the binder is low (Gaedcke, 1993). These pigments are widely used in water-repellent stains on wood, particularly in Scandinavia. Being transparent they enable the wood grain to be seen while still providing protection against detrimental effects of exposure to sunlight or even fluorescent light. UV light penetrates wood surfaces (to a depth of ca. 75 μ m) and causes decomposition of the lignin and hence, cell breakdown; this in turn leads to enhanced water uptake followed by cracking and discolouration. The iron oxide stain counter-

acts this effect (Sharrock, 1990). These stains also have the advantage of being light fast, chemically resistant and economical; only 2% by weight of pigment in the stain is required. Owing to their high UV adsorption, transparent iron oxides are also used to colour plastic films and bottles used for packaging UV sensitive food. Another major application is in metallic paints in combination with thin flakes of aluminium. A coating of transparent Fe oxide over metal produces a brilliant gold or copper colour; it is used for colouring metal furniture, gold coloured, metal cans and the production of simulated brass handles.

Synthetic MIO is used in primers as well as in topcoat paints; the natural MIO was too coarse for use in undercoats. Weathering tests with different paint binders indicated that the performance of the synthetic product was as good or better than, that of the natural product (Carter and Laundon, 1990). The aspect ratio of MIO produced by hydrothermal synthesis can be altered by doping with Al, Mn or Si, thus enabling a more lustrous material with a reddish-brown colour to be produced; this material is suitable for decorative as well as for purely protective purposes (Pfaff and Reynnders, 1999).

Interference (or metallic) pigments consist of mica platelets 200–500 nm in thickness upon which thin layers (50–150 nm) of transparent hematite particles have been deposited by precipitation of Fe^{III} oxide from an aqueous Fe^{II} or Fe^{III} salt solution, followed by calcination at 700–900 °C. These pigments are light-fast, corrosion-resistant and brilliantly coloured. The colour changes due to interference effects, from bronze, through copper, red, red-violet and red-green as the thickness of the metal oxide layer increases (Franz et al., 1993). A feature of the paints is the change in colour from deep red to green as the angle of viewing alters; the actual colours observed in this “lustre flop” depend to some extent on the thickness of the hematite layer. In addition, the paints have a pearly or iridescent appearance. They are used on automobiles. Such paints are relatively expensive, but are still far cheaper than the organic pigment based paints which perform the same function. Brilliant red-gold or green-gold (depending on the method of precipitation), interference pigments arise when hematite particles are combined with TiO_2 on mica plates; these pigments are used in cosmetics and printing ink.

The mixed iron oxides, e.g. $(\text{Fe}, \text{Mn})_2\text{O}_3$ and ZnFe_2O_4 have bixbyite, corundum or spinel structures. The most important of these mixed oxides is the zinc ferrite (spinel structure), a tan pigment which is used for colouring plastic, particularly for yellow rubbish bags. In parts of the U.S.A. it is used to colour roof shingles. This ferrite is thermally stable and maintains its colour at relatively high temperatures. Hematite may be heated with zinc oxide to produce zinc ferrite which is used as an anticorrosion pigment.

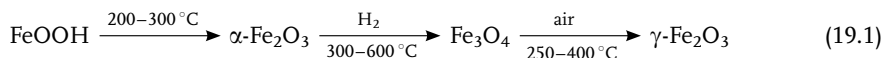
19.3

Magnetic pigments

Magnetic pigments have been used in electronic recording devices since the late 1940's. Its moderate cost and chemical stability make maghemite, $\gamma\text{-Fe}_2\text{O}_3$, the principal magnetic pigment. Even though it displays high magnetization and coercivity

(see Chap. 6), magnetite, Fe_3O_4 , is less suitable for recording devices owing, to its magnetic instability (Sharrock and Bodnar, 1985). As magnetic pigments must be of very high purity ($> 99.5\%$ $\gamma\text{-Fe}_2\text{O}_3$), they are always produced synthetically.

For recording devices, needle-shaped particles ensure the best magnetic properties, particularly a high coercive field strength (H_c). For maghemite, $H_c = 20\text{--}35 \text{ kA m}^{-1}$. Because maghemite normally consists of isometric crystals, it must be produced in a series of steps from acicular FeOOH in order to obtain a needlelike morphology. In this process (acicular), goethite or lepidocrocite is dehydroxylated to hematite and then reduced to magnetite and finally reoxidized to maghemite (see Chap. 20), i.e.



It is also possible to produce acicular hematite from ferrihydrite by using suitable additives, thus avoiding the dehydration step and hence pore formation (Matsumoto et al., 1980). The hematite is then stabilized against sintering during subsequent thermal treatment by being coated with silicate or phosphate so that the acicular shape is maintained throughout the whole process. The resulting maghemite has a length to width ratio of between 5:1 to 20:1.

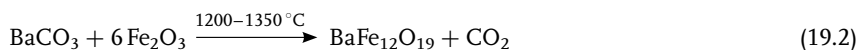
Particles with lengths of ca. $0.6 \mu\text{m}$ are used in computer tapes: these account for 25% of the acicular maghemite that is produced. Other applications of this material include low bias audio cassettes and studio and broadcasting tapes.

Maghemite is often doped or coated with up to 5% Co in order to improve coercivity and storage capacity; H_c of cobalt-doped maghemite is $40\text{--}75 \text{ kA m}^{-1}$. Such doped pigments compete successfully on these grounds with CrO_2 for use in video tapes, high bias audio tapes and floppy discs. They are also cheaper. Coated pigments have greater thermal stability than their doped counterparts and display uniaxial magnetic anisotropy (Sharrock and Bodnar, 1985).

Some magnetic pigments (99% Fe_3O_4) are used in magnetic ink character recognition (MICR) devices, e.g. inks and toners in photocopying and facsimile machines and also in security inks. For high resolution toners, spherical magnetite particles ($0.1\text{--}0.3 \mu\text{m}$) are required; in some cases, the surfaces of these particles are modified with silanes or polymers. Superparamagnetic Fe_3O_4 is used in metallography for detecting flaws in engines.

19.4 Ferrites

Iron oxides and hydroxides are used as the starting material in the production of ferrites. Hard ferrites (high coercivity) e.g. $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$ are made from hematite by a sintering process, i.e.



Barium ferrites form brown, hexagonal crystals with extremely uniform magnetic properties which can be reproducibly controlled by optimising the production conditions. They are used in ceramic permanent magnets, in high density, digital storage material and as anti-forgery devices in the magnetic strips of cheque and identity cards. A further use for these materials may be as “hot sources” for the treatment of certain tumours (Jones et al., 1992). Iron oxides are the precursor materials of soft ferrites such as (Mn, Ni)Fe₂O₄ and (Zn, Mn)Fe₂O₄.

19.5

Catalysts

Iron oxides serve as catalysts (or as the starting materials for catalysts) for various industrial syntheses. Inorganic processes which use these catalysts include synthesis of NH₃ (the Haber Process), the high temperature water gas (CO + H₂O) shift reaction for the production of hydrogen and the desulphurisation of natural gas. Organic syntheses include dehydrogenation of ethyl benzene to styrene, the Fischer-Tropsch synthesis of a range of hydrocarbons from hydrogen and carbon monoxide, oxidation of alcohols to aldehydes and ketones and the large scale manufacture of butadiene to produce elastomers (Table 19.3). These are all heterogeneous reactions with the solid phase reacting with the gaseous or liquid reagents.

The principal iron oxides used in catalysis of industrial reactions are magnetite and hematite. Both are semiconductors and can catalyse oxidation/reduction reactions. Owing to their amphoteric properties, they can also be used as acid/base catalysts. The catalysts are used as finely divided powders or as porous solids with a high ratio of surface area to volume. Such catalysts must be durable with a life expectancy of some years. To achieve these requirements, the iron oxide is most frequently dis-

Tab. 19.3 Industrial synthesis reactions involving iron oxide catalysts.

Reaction	Catalyst or catalyst precursor
Synthesis of ammonia $N_2 + 3 H_2 \rightarrow 2 NH_3$	Fe ₃ O ₄ promoted with Al ₂ O ₃ /K ₂ O/CaO
Water gas shift reaction $CO + H_2O \rightarrow H_2 + CO_2$	Fe ₃ O ₄ /Cr ₂ O ₃
Fischer-Tropsch synthesis $CO + H_2 \rightarrow \text{hydrocarbons} + H_2O$	Fe ₃ O ₄ /5–10% Cr ₂ O ₃ Hematite promoted with SiO ₂ /K ₂ O
Dehydrogenation of ethylbenzene to styrene	Hematite/K ₂ O
Vapour phase oxidation of alcohols to aldehydes and ketones	Hematite/MoO ₃
Liquefaction of H ₂ to 100% parahydrogen	“Hydrated” iron oxides
Steam gasification of brown coal ^{a)}	Ultrafine FeOOH

a) Yamashita et al. (1991)

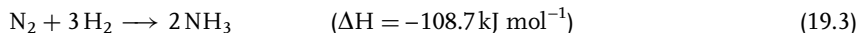
persed on a supporting material (e.g. SiO_2 , MgO or Al_2O_3) and mixed with one or more promoters, usually K_2O or CaO . Promoters are additives which maximize the surface area of the catalyst and enhance its resistance to poisoning and thermal deactivation (Bond, 1974).

A characteristic of catalysis processes is that a variety of compounds may catalyse a particular reaction, but only one or two of these catalysts show enough selectivity, activity and stability to warrant use in an industrial process. Selectivity is the ability of a catalyst to increase the relative rate of formation of a desired product when two or more competing reactions may occur. For modification of the direction of a reaction, mixed catalysts consisting of two compounds both with moderate to good catalytic activity have been developed. For example, the vapour phase oxidation of alcohols to aldehydes and ketones involves a mixed $\alpha\text{-Fe}_2\text{O}_3/\text{MoO}_3$ catalyst rather than a single oxide.

In some major reactions, the iron oxide is the starting material for the actual catalyst which is active iron metal. Quite often both the metal and its oxide can catalyse the reaction, but the activity and selectivity of the metal is greater. Furthermore, the oxide catalyst may be reduced to some intermediate product during the reaction, particularly a reaction involving H_2 and high temperature. This may lead to loss of catalytic activity as the intermediate may be a less suitable catalyst than the starting oxide or the actual metal. To avoid this occurrence, the oxide is frequently “prereduced”, i.e. converted to the metal by a thermal/reduction pretreatment in a preliminary step.

Two of the most intensively studied industrial syntheses involving iron oxides as catalysts are the Haber process for the production of NH_3 from hydrogen and nitrogen, and the Fischer-Tropsch synthesis of hydrocarbons. A third process, the water gas shift reaction which produces hydrogen from carbon monoxide and water, is often a pre-step for NH_3 synthesis. The pre-step reaction uses magnetite as the catalyst. Magnetite is cheap, stable and can withstand a high level of impurities without being poisoned. As, however, it requires temperatures in excess of 350°C in order to have sufficient activity for commercial applications, it is mixed with chromium oxide in order to stabilise it during the reaction (Campbell et al., 1970).

NH_3 is used mainly for fertilizer production and, to a lesser extent, for making nitric acid. It is synthesised on a large scale by the *Haber Process*, i.e.



The reaction is exothermic, hence the highest equilibrium yield is obtained at low temperatures and high pressures. The catalyst functions by inducing the formation of a nitrogen complex with the catalyst surface; this complex is far more readily hydrogenated to NH_3 than is nitrogen with its triple bond (Somorjai and Salmeron, 1986).

Most catalysts for NH_3 synthesis are based on magnetite (from natural sources) to which a few percent of Al_2O_3 and various other promoters are added and fused together. This catalyst was developed in Germany between 1905 and 1910 and has been used industrially since 1914 (Topham, 1985). Singly *promoted* catalysts contain only Al_2O_3 , whereas doubly promoted catalysts contain K_2O as well. In addition, there are low levels of a number of other additives, some of which originated as impurities in the original ore and were found to enhance the activity of the catalyst

(Bridger and Snowden, 1970). Before the magnetite is reduced to (mainly) iron, it is fused with the promoters at 1600 °C to give a low area, non porous Al-magnetite with K₂O located at the grain boundaries of the magnetite crystals. The fused catalyst is then reduced with H₂ or a mixture of H₂ and CO (synthesis gas) to give a porous α -Fe matrix with a surface area of 10–25 m²g⁻¹. The structural promoter (Al₂O₃) is distributed over the surface of the Fe particles and stabilises them against sintering and thus a reduction of surface area during the operation of the catalyst. K₂O acts as an electronic promoter (i.e. changes the electronegativity of the external surface) and facilitates the chemisorption of N₂.

The *Fischer-Tropsch* synthesis involves a reaction between H₂ and CO at 200–300 °C and under pressure; it produces a range of reaction products. An iron oxide based catalyst leads to various straight chain acids, alcohols and aldehydes. The synthesis is carried out on an industrial scale by the South African plant of Sasol with SiO₂ promoted hematite as the catalyst. During the synthesis process, the iron oxide catalyst changes with the working catalyst becoming a mixture of iron carbide, hematite and magnetite; the proportions of the different iron oxides depend upon the operating conditions (Wang and Davis (1999) and references therein).

Laboratory studies have indicated an increasing number of further processes for which iron oxides may be used as catalysts. A sodium promoted iron oxide on a support of SiO₂ catalyses the gas phase oxidation (377–427 °C) by nitrous oxide, of propene to propene oxide (Duma and Honicke, 2000). Ferrihydrite or akaganéite can be used to catalyse the reduction (at 55–75 °C) by hydrazine, of aromatic nitro compounds to aromatic amines (which are the starting materials for a huge range of chemicals): these Fe oxides have the potential to provide a safe and economical pathway to the production of these important organics (Lauwiner et al., 1998).

Gold catalysts, prepared by using ferrihydrite as a support for the gold-phosphine complex, Au(PPH₃)(NO₃), are very active towards oxidation of carbon monoxide at –73 °C (Kozlova et al., 1998). Iron oxides can also be used to catalyse the degradation of acrylnitrile-butadiene-styrene copolymer (an important constituent of municipal waste) into fuel oil. The effect of maghemite, magnetite/carbon composites and goethite, in reducing the amount of (undesirable) N₂ in the fuel oil has been investigated and the change in the structure and composition of the goethite catalyst with temperature has also been monitored (Brebou et al., 2000, 2000a). Sulphation of Fe oxide catalysts suppressed low temperature (< 400 °C) oxidation of methane, but enhanced the production of methanol and ethane at 500 °C (Brown et al., 1998).

Goethite (surface area 50 m² g⁻¹) has been reported to catalyse the hydrolysis of carboxylate and phosphorothioate esters (Torrents and Stone, 1994). The authors suggest that the sulphur of the thioester binds to the surface Fe of the goethite and thereby reduces the electron density at the P atom which in turn facilitates the nucleophilic attack by OH and promotes hydrolysis.

Another Fe oxide catalyst with the trade name Nanocat[®] is produced by oxidizing a diluted gaseous iron-containing compound (iron pentacarbonyl) in a heated, oxygen-containing gas-phase. It is used as a burning-rate catalyst for solid rocket fuels (oxidation of NH₄ClO₄). It consists of 2-line ferrihydrite either pure or admixed with some hematite (Fig. 19.1) and has an average particle size of 3 nm and a surface area of

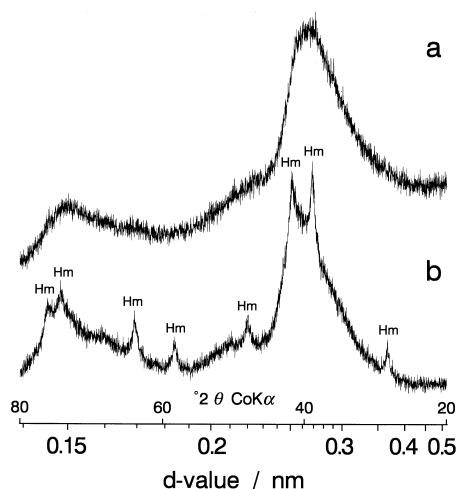


Fig. 19.1. X-ray diffractograms of two lots of an Fe oxide catalyst (Nanocat[®]) consisting of 2-line ferrihydrite (a) and a mixture of this with hematite (b).

around $200 \text{ m}^2 \text{ g}^{-1}$ (Zhao et al., 1993; Feng et al., 1993; Kosowski, 1993). The catalyst can also be used in coal liquefaction (Huffman et al., 1993) and as an ultraviolet energy absorber. Ferrihydrite (2-line) precipitated from aqueous Fe^{III} salt solutions has also been investigated for its suitability as a catalyst. The problem with this material is that it quickly agglomerates and transforms to hematite on heating, thereby losing much of its active surface. This can be avoided by adding crystallisation inhibitors such as Si, Al (Zhao et al., 1994a), Mo (Zhao et al., 1994b) and citric acid (Zhao et al., 1994c). These results are based on earlier observations of the inhibitory effect of the above additives (see Chap. 14). Ferrihydrite has also been used as a precursor of a pyrrhotite (Fe_{1-x}S) catalyst during direct coal liquefaction (Zhao et al., 1995).

19.6

Other uses of iron oxides

Owing to their hardness, magnetite and hematite have been used as *abrasives* and *polishing agents*. Emery, for example, is a mixture of corundum and magnetite: its hardness (7.5–9) depends on the corundum content. It is used as an abrasive in grinding wheels, in emery paper and for rough grinding of glass. Jewellers' rouge is a lightly calcined form of hematite that is used to polish gold and silver and crocus, a more strongly calcined hematite, is used for polishing brass and steel. Hematite is also used to produce a high lustre on the gilding on porcelain. In earlier times, polishing rouge was used by the plate glass industry, but owing to changes in the technology, its use has declined considerably.

Thermite welding is used for joining iron rails and also for liberating elements such as W and V from their oxides. The welding process involves heating a mixture of aluminium powder and hematite (thermite); the vigorous reaction which results produces Al_2O_3 and iron, i.e.



The hematite is reduced to white hot, liquid iron which is poured into a mould enclosing the join between the rails.

Ferrofluids are magnetic fluids (i.e. liquid magnets) that contain nanometre sized magnetic iron oxide particles in aqueous or organic media. Such fluids exhibit a high degree of colloidal stability in a magnetic field gradient. Since they were first developed, ferrofluids have found ever increasing application in the field of engineering (Raj and Moskowitz, 1990). They are used as dynamic process seals in X-ray machines, lasers and certain furnaces where they provide a reliable, hermetic seal. As exclusion seals which protect sensitive mechanical or electronic parts from contamination, ferrofluids are used in the rotating joints of clean room robots, in machines for the textile industry and in some computer peripherals. They are also used in NMR probes for oil prospecting and to study the domain structure in magnetic tapes; in the latter case, the particles in the ferrofluid congregate at the magnetic domain boundaries, thus enabling them to be seen (under an optical microscope) and their widths estimated.

Hematite is used to coat the red emitting phosphor, $\text{Y}_2\text{O}_3\text{Eu}$, which is used in *cathode ray tubes* (Franz et al., 1993; Merckhi and Feldmann, 2000). Hematite is also used in *sensors* for the detection of hydrocarbon gases and carbon monoxide. The sensitivity of the sensor can be improved by sintering the oxide with $0.09 \text{ mol}^{-10} \text{ mol}^{-1} \text{ Al}$ at 850°C (Han et al., 2001 and references therein).

Goethite is used in *flame retardants* and *smoke suppressants*. Both laboratory and large scale pilot tests showed that goethite is the most active smoke suppressant when polymers and plastics are burned (Carty and White, 1999; Carty et al., 1999). It reduces the amount of smoke produced during pyrolysis in air of chlorinated PVC plasticized with dioctylphthalate, by changing the decomposition pathway followed by phthalate, so that benzene, which is produced in the absence of the smoke suppressant, is not formed (Carty et al., 1999).

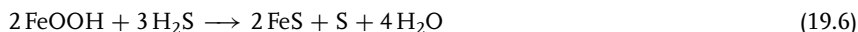
The airbags in automobiles contain hematite which serves as a catalyst for the rapid release of N_2 which inflates the bags (G. Buxbaum, pers. comm.).

Iron oxides are used in the manufacture of *sulphate-resisting cements* and as an additive in the production of Portland cement. In the latter, iron oxides promote the formation of calcium silicates in the flux and this lowers the temperature required to burn clinker and prolongs the life of the kiln (Pettifer, 1981). Hematite and magnetite (as ores) are used as high density coatings for concrete seabed pipelines that bring oil and gas to shore (Pettifer, 1981). These coatings stabilize the pipelines on the sea floor and provide protection against physical damage.

Magnetite is used as the dense material in mineral separation processes, the most important of which is the *washing of coal* (Pettifer, 1981). These processes involve use of a washing fluid of appropriate specific gravity (consisting of the requisite amount of finely ground magnetite and water) to divide mineral fractions with different specific gravities. Magnetite is particularly suitable for this application owing, above all, to its high specific gravity (5.18) and also its hardness, chemical stability and low cost. A further important factor is its magnetism which facilitates recovery after pro-

cessing by magnetic separators. Use of magnetite in coal washing is increasing because, as the industry becomes increasingly mechanised, more rock (i.e. waste) is dug out with the coal.

Iron oxides are used as the *flux in smelting of nonferrous metals* (e.g. lead) (Pettifer, 1981). The oxide removes the siliceous and other impurities and also serves to keep the slag fluid. A further use of iron oxides (FeOOH) is in the *removal of H_2S* from coal gas, i.e.



Owing to their high surface area and affinity for many ions, Fe oxides are used in *water treatment* processes (see Chap. 21). Coprecipitation of radionuclides with Fe^{III} oxides at $\text{pH} > 10$ can be used to decontaminate low level, radioactive waste.

Iron oxides have various application in *medicine*. They have been tested for use in hyperthermia of cancers, i.e. they form part of the ferrimagnetic material which is injected into the vicinity of the tumour and, in response to the application of an alternating magnetic field, heats and destroys the tumour; the technique appears to have the potential to destroy deep-seated tumours (Kawashita et al., 2001 and references therein). Super-paramagnetic magnetite is used as the core in magnetic resonance imaging (MRI) contrast agents which are used to differentiate between healthy and diseased tissue (Babes et al., 1999). A novel use of maghemite is in a radiation free method of measuring the rate of gastric emptying in patients (Forsman, 1998). Ferrihydrite may find an application in radiation synovectomy, a technique used to reduce the pain associated with arthritis (Pirich et al., 2000).

19.7

Undesirable iron oxides

Iron oxides are non beneficial and may even be undesirable in certain situations. Probably the best known example of this is their presence in the corrosion products of iron and steel (see Chap. 18). Iron oxides are also produced as mostly unusable byproducts of the extraction of nonferrous metals. Iron is present in the ores of Cu, Ni, Zn, Pb, Al, Mn and Ti and has to be eliminated (as iron oxides or jarosite) during processing. An example of this comes from the aluminium industry in which gibbsite ($\text{Al}(\text{OH})_3$) is produced from bauxite via dissolution in alkaline solution (Bayer process). Goethite and hematite are the principal iron containing constituents of bauxite (Valeton, 1972). As these oxides are Al-substituted, their presence reduces the amount of Al that is extracted, and if Fe contaminates gibbsite, the quality of the aluminium produced can be affected. Iron oxides are removed from the production circuit before precipitation of gibbsite; they are sedimented in clarification tanks with flocculating agents (red mud) (see Chap. 10). Fine particle goethite impedes settling of the sediments, so where possible, goethite is converted to the denser he-

matite during the digestion of the bauxite. The bulk of the red mud that leaves the clarification tanks is held in storage tanks as wastes. Disposal of red muds is a problem, worldwide. Only a small amount of mud is used for soil amelioration; the high alkalinity prevents wider use. Efforts to produce marketable pigments have proved uneconomic and attempts to reduce the volume of storage space required have, to date, been unsuccessful.

There are various other examples of unwanted occurrences of iron oxides. Iron oxides hinder extraction of Cu, Ni, Co and Mn from manganese nodules. Large quantities of ferrihydrite are produced during the extraction of Ni from Ni ores with NH_4OH at elevated temperatures. Iron oxides are also undesirable contaminants of china clay where their presence detracts from the pure white colour of porcelain products. Dithionite is used as a reductant to bleach kaolin (Jepson, 1988). Iron oxides are impurities in glass making, with even low levels of the impurity giving glass a blue-green tint.

Iron oxides often contaminate water supplies and have to be removed in water processing plants. In Finland, for example, increasing demand for drinking water has led to purging of unoxidized ground water too high in Fe^{2+} ($1\text{--}23\text{ mg L}^{-1}$) and Mn^{2+} for normal use. Deferration is achieved by overland flow or, more recently, by slow sand infiltration or re-infiltration (Hatva, 1989). The Fe oxide which accumulates is usually ferrihydrite (Carlson and Schwertmann, 1987). Blocking of drain pipes by iron oxides, in soils with Fe^{2+} containing groundwater has been described in Chapter 15 (Plate 15.V, see p. XXVIII). Reductive dissolution of arsenic containing Fe^{III} oxides is considered to be responsible for the arsenic present in the ground waters and wells in parts of Bangladesh (Hug et al., 2001 and references therein). Unsightly orange stains on walls and pavements are often the result of watering lawns with Fe containing water. Iron overload diseases lead to deposits of unwanted iron oxides in body tissues (see Chap. 17). U.S. scientists have reported that laboratory dust can contain high levels of magnetite which may interfere in electromagnetic field studies (Kobayashi and Kirschvink, 1995).

20

Synthesis

20.1

Industrial synthesis

20.1.1

General

Industrial syntheses are concerned primarily with producing iron oxides for use as paint or magnetic pigments or as chemicals. The purity of the product ranges from around 97% for certain paint pigments up to 99.99% for magnetic pigments. Particularly for paint pigments the synthesis process must give a product with carefully controlled properties viz. particle size, size distribution and morphology, all of which influence the colour and dispersibility in the paint vehicle. Economic factors are important, particularly the cost of raw materials, markets for byproducts and the disposal of waste products in accordance with environmental regulations.¹⁾ The starting materials for iron oxide synthesis are almost always Fe^{II} salts rather than Fe^{III} salts, because the former are much cheaper. The Fe^{III} salts are used only in hydrothermal syntheses for production of high value products.

The synthesis route chosen for a particular product is governed by all the above considerations. There are three major synthesis methods for industrial pigments:

1. Solid state transformations including thermal decomposition of iron salts and oxide-hydroxides. This method produces red, black and brown pigments.²⁾
2. The organic reduction process also termed the aniline, laux or nitrobenzene process. This method leads to black, yellow or red pigments.
3. Precipitation of soluble Fe^{II} salts with alkali followed by oxidation. There are two variations of this method. The pigments obtained may be yellow, red, orange or black.

Other methods including hydrothermal precipitation, flame hydrolysis, thermal decomposition of $\text{Fe}(\text{CO})_5$ and high temperature reaction of Fe^{III} chloride with iron, are used only on a small scale to obtain specialty products (see Chap. 19).

1) The Bayer Pigment factory at Krefeld (FRG) installed a waste water treatment plant in the 1960s, well ahead of the environmental requirements of the day.

2) It must be noted that the pigments are referred to in the industry by colour rather than by composition. However, in this chapter the usage in the rest of the book is followed and mineral names are used.

Full details of the different industrial syntheses are provided in the Kirk-Othmer Encyclopaedia of Chemical Technology (1982), Ullmann's Encyclopaedia of Industrial Chemistry (1992, and references therein) and in Buxbaum and Printzen (1993).

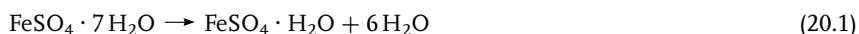
20.1.2

Solid state transformations

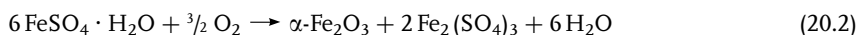
This process involves heating selected iron oxides or iron salts in rotary kilns in an oxidizing atmosphere. The resulting pigment is first suspended in water, filtered, washed and dried. It is then ground to the appropriate size in a mill (jet, pendular or pin). The starting materials may be $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (copperas), FeCl_2 , FeCl_3 , all iron oxide hydroxides, iron carbonate or magnetite.

20.1.2.1 The copperas process

This process is used particularly in the USA. Copperas is a byproduct of the sulphate process used to produce TiO_2 and from the steel industry (i.e. spent pickle liquors) and is named after its green-blue colour which resembles that of copper compounds. Although copperas can be transformed to hematite in a one stage process, the resulting pigment is of poor quality; a two stage transformation is, therefore, used. The first stage involves recrystallization of the copperas to give a compound with a low level of impurities, i.e. Cu, Mn and other heavy metals. This is then dehydrated to the monohydrate form:



In the second stage the monohydrate is calcined at 650°C to produce hematite:

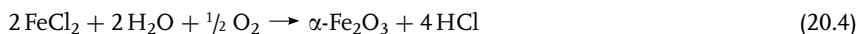


The product, which is termed "copperas red" is a high quality, hard, red pigment.

If alkaline earth oxides or carbonates are present during calcination, the iron sulphate can be reduced with carbon-containing compounds to sulphur dioxide which can then be oxidized with air to sulphuric acid. The copperas process, thus, has the advantage of producing a saleable by-product; a disadvantage of this process, however, is the production of the waste gases and soluble impurities which must be disposed of in an environmentally safe manner.

20.1.2.2 Other solid state processes

Other iron salts, for example FeCl_2 can be transformed at high temperatures in air into a low quality hematite, i.e.



Calcination of iron salts under reducing conditions gives magnetite with high tinting strength. This process produces undesirable furnace gases. Controlled high temperature heating of magnetite under oxidizing conditions leads to hematites with a range of red shades. The hematite retains the cubic morphology of the precursor. This reaction is self-sustaining and hence, is difficult to control.



Controlled oxidation of magnetite at 500 °C gives maghemite, i. e.



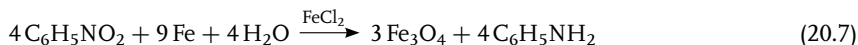
Dehydroxylation of goethite produces the “ferrite reds” – extremely colour fast and pure hematite. With low temperature calcination the acicular shape of the goethite precursor is retained, whereas high temperatures lead to a sintered product.

Micaceous iron oxides are produced in a process which involves heating FeCl_3 and iron at 500–1000 °C to form molten Fe^{III} complexes which are then oxidized to micaceous hematite; the diameter of the plates can be varied from 5 to 75 μm depending on whether the oxide is intended for use in a primer paint or a topcoat (Carter, 1988).

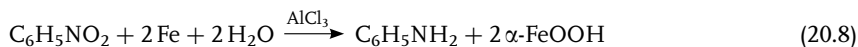
20.1.3

Reduction of organic compounds

This process is used principally in Europe. It was first developed in 1854 for the production of aniline. Nitrobenzene was reduced to aniline using metallic iron, hence the process was termed the aniline or nitrobenzene process. Iron oxides were formed as unusable, grey/black products. Around 1925, Laux found that addition of iron chloride modified the process so that iron oxides suitable for use as pigments could be produced. With this additive alone, magnetite with a high tinting strength results, i. e.



Addition of other hydrolyzable tri- or tetravalent metal ions, particularly Al^{III} directs the product to goethite, i. e.



Enough heat is generated by the reaction to keep the suspension at boiling point. It is essential to have an excess of iron metal to ensure complete decomposition of the nitrobenzene. The details of the reaction mechanism are not fully understood, but it is presumed that the nitrobenzene oxidizes Fe^{II} to Fe^{III} which is then hydrolysed. The acid is released by hydrolysis and pigment formation and dissolves the metallic iron and thus renews the supply of Fe^{2+} ; no additional acid other than that produced dur-

ing the process is required for dissolution of the iron and in addition, no alkali (for hydrolysis) need be added to the system. The reaction is self perpetuating.

At the completion of the reaction, the aniline is separated from the iron oxides by steam distillation and the unreacted iron removed. The pigment is washed, filtered and dried, or calcined in rotary kilns to hematite (Plate 20.I, see p. XXXIX). Considerable control over pigment properties can be achieved in this process by varying the nature and concentration of the additives and the reaction rate; the latter depends on pH, the rate of addition of iron and nitrobenzene and the type and particle size of the iron particles. Two advantages of this method are that a saleable byproduct, aniline, is produced and that there are no environmentally, harmful waste products.

20.1.4

Precipitation from Fe^{II} solutions

Basically, this process involves neutralisation of the Fe^{II} salt solution to bring the pH into the slightly acid to slightly alkaline range (depending upon the product required) followed by oxidation with air. This is a batch process and is carried out in large tanks open to the atmosphere (Plate 20.II, see p. XXXIX). The reaction product is governed mainly by the pH (i.e. the Fe: OH mole ratio) and the temperature of the suspension. For yellow pigments (goethite), the suspension pH is maintained in the acid region and the temperature varied from 10–90 °C, a temperature range over which the reaction time decreases from 100 to 10 h. The colour and uniformity of the product can be improved if seed crystals (10–30 nm) produced in a separate process are added to the suspension. Following precipitation and growth (which may take from hours to weeks depending on the pigment properties required), the pigments are washed and dried in rotary kilns.

Lepidocrocite can be obtained by precipitating the Fe^{II} ions at almost neutral pH and subjecting the resulting suspension to a brief heating/rapid cooling stage followed by oxidation. If precipitation, followed by aeration, is carried out at 90 °C and pH > 7, magnetite with a good tinting strength is obtained. This pigment can also be produced by heating a mixed Fe^{II}/Fe^{III} suspension at 90 °C. Hematite can be precipitated by this method if the Fe^{II} salt is reacted with an excess of alkali (often in the presence of small amounts of directing cations) at 65–90 °C and then oxidized with air. Alternatively, the Fe^{II} salt may be added to the hematite seeds continuously and the suspension oxidized at 80 °C.

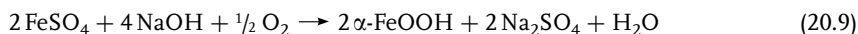
The raw materials for this process are FeSO₄ · 7 H₂O or FeCl₂ (byproducts from TiO₂ production or steel-pickling), alkali (NaOH, Ca(OH)₂, ammonia or magnesite) and, for the Penniman process, scrap iron as well. When pickling-liquors are the source of iron salts, the free acid they contain must first be neutralized by reaction with scrap iron. It is essential that the iron is free from alloying elements and that any impurity salts in the iron sulphate are removed by partial precipitation; otherwise pigment properties are affected adversely. A disadvantage of this process is the precipitation of soluble salt (e.g. Na₂SO₄, NaCl) as waste products.

The precipitation process serves to produce soft, yellow, orange, black or red iron oxides with very pure hues and good wetting properties. In contrast to the solid state

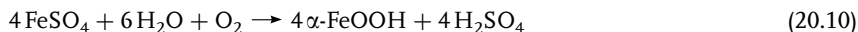
processes, good control of crystal shape and particle size distribution can be achieved. Parameters that directly affect the composition and properties of the product are the pH, suspension viscosity, rate of aeration of the suspension and oxidation rate. Other parameters with an indirect influence are the concentration of Fe^{II} salts, the type of anion (sulphate or chloride), temperature, the oxidizing agent, any modifiers or directing agents and the rate of agitation. Engineering considerations, for example the size and shape of the reaction vessel and the geometry of the stirrer, can also have a marked influence on the properties of the product.

The *Penniman process* (1917) from the U.S. is a modification of the precipitation process which, owing to the use of metallic iron as one of the reagents, is extremely economical of reagents and equally importantly, reduces the level of soluble waste salts. It is the process used most widely for goethite production.

The process involves seeding tanks containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution, alkali and metallic iron with FeOOH , and aerating the stirred suspension. The seeds, which are very fine, are precipitated from Fe^{II} solution at $20\text{--}50^\circ\text{C}$ (depending on the colour required), i.e.



They can be used as transparent pigments, but to develop hiding power they have to grow to a larger size. In the growth tank, the reaction is carried out at $75\text{--}90^\circ\text{C}$, i.e.



The sulphuric acid that forms interacts with the (scrap) iron to replenish the supply of Fe^{2+} ; this reaction is one of the advantages of the process – only small amounts of Fe^{II} sulphate and alkali are needed to initiate the reaction. The reaction time varies from two days to several weeks depending on the pigment being produced and the size required for the particles.

20.1.5

Other processes

Thermal decomposition of iron pentacarbonyl. Very finely divided red iron oxide is obtained by atomizing iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, and burning it in excess of air. The size of the particles depends on the temperature ($580\text{--}800^\circ\text{C}$) and the residence time in the reactor. The smallest particles are transparent and consist of 2-line ferrihydrite, whereas the larger, semi-transparent particles consist of hematite (see Chap. 19). The only byproduct of the reaction is carbon dioxide, hence, the process has no undesirable environmental side effects. Magnetite can be produced by the same process if it is carried out at $100\text{--}400^\circ\text{C}$. Thermal decomposition of iron pentacarbonyl is also used to coat aluminium powder (in a fluidized bed) and also mica platelets with iron oxides to produce interference or nacreous pigments.

Hydrothermal processes, i.e. the heating of suspensions of ferrihydrite in alkaline media under pressure, have been used to produce large platy crystals of hematite. This process gives well formed crystals, but is expensive. The crystals can be reduced to produce isomorphous magnetite plates. *Flame hydrolysis* involves burning Fe^{III} chloride at 400–800 °C to iron oxide. Owing to the many technical difficulties associated with this process, it is not commercially important.

Iron is a common impurity in many hydrometallurgical processes including the refining of zinc. After the roasted zinc ore (calcine) has been leached in sulphuric acid to produce ZnSO_4 solution (from which the zinc is obtained by electrolysis), the iron accumulates as an insoluble zinc ferrite in the residue. This residue can be dissolved in hot, concentrated H_2SO_4 to recover more zinc and the dissolved iron is stabilised by precipitation as jarosite (the *Jarosite process*), goethite (the *Goethite process*) or (rarely) as hematite (Dutrizac, 1987). The goethite process is economical and produces a compact residue, but the goethite is contaminated with sulphate and with various elements such as Sb and Ga which limits the opportunity for disposal. In the *Hematite process*, the hot leach solution is reduced with SO_2 gas or ZnS to bring the iron into the Fe^{II} form, neutralized with limestone or calcine and the Fe^{II} oxidised/hydrolysed in an autoclave at 200 °C to hematite. The advantage of hematite is that it can reduce residue volumes by more than 50%, but the process is expensive. The hematite is contaminated with Zn and sulphate and so is unsuitable for use in the steel industry. Laboratory studies have shown that a solvent extraction process could overcome the impurity problem and enable “clean” hematite to be produced (Dutrizac, 1996).

20.1.6

Magnetic pigments

Use of maghemite in magnetic recording devices requires that, to ensure good magnetic properties, this compound has an acicular morphology. This is achieved by using goethite or lepidocrocite as the starting material. A very pure FeOOH is needed because even low levels of impurities impair the magnetic properties of the product.

The first stage in the process is thermal dehydroxylation of FeOOH to hematite. The FeOOH is stabilized against thermal stress (and possible morphological changes due to sintering or outgrowths) by a coating of silicate, phosphate, chromate or organic fatty acid. The hematite is then reduced at 350–600 °C to magnetite with the aid of H_2 , CO or organic compounds while maintaining its acicular shape. Finally, the magnetite is oxidized at 200–500 °C to maghemite:



In some instances acicular hematite crystals are produced hydrothermally from ferrihydrite in the presence of citrate or phosphate and converted to magnetite and

thence, maghemite. The magnetic properties of maghemite are improved by doping with up to 5% cobalt. This is effected either by coprecipitation of cobalt hydroxide with the FeOOH precursor or by precipitation of a coating of Co(OH)_2 on the maghemite particles after they have been formed.

20.2

Laboratory synthesis methods

A great variety of methods for the synthesis of each iron oxide exists. Reliable, convenient methods of producing the various iron oxides are already available (Schwertmann and Cornell, 2000). This chapter, therefore, describes one reliable method for each oxide in some detail and then briefly enumerates other methods; full details of the latter methods can be found in each accompanying reference.

20.2.1

Goethite

Precipitate ferrihydrite by adding 180 mL 5 M KOH to 100 mL M $\text{Fe(NO}_3)_3$ solution. Dilute the suspension to 2 L with bidistilled water and hold in a closed polypropylene flask in a 70 °C oven for 60 h. During this time the voluminous redbrown ferrihydrite suspension transforms into a compact yellow precipitate of goethite. Wash well and dry at 50 °C. Around 9 g goethite should be obtained.

Other methods

1. Air oxidation at room temperature (RT) of a 0.0454 M FeCl_2 solution (buffered with NaHCO_3 and previously outgassed with N_2) until the greenish colour of the suspension is replaced by a yellow precipitate (some hours). The product is rather poorly crystallized (Schwertmann and Cornell, 2000).
2. Oxidation of a hot FeSO_4 solution with a mixed $\text{NaOCl/Na}_2\text{CO}_3$ solution. This gives a poorly crystallized material (Duvigneaud and Derie, 1980).
3. Dialysis for 6 months at RT of M $\text{Fe(NO}_3)_3$ solution against bidistilled water of pH 5. This gives a mixture of polymeric particles and uniform, rod-like crystals of goethite. The goethite can be separated from the polymer by gel chromatography using a Sephadex 200 substrate (Van der Woude and de Bruyn, 1984).
4. Reaction at 85 °C of Fe^{III} sulphate solution (buffered at pH 6 with sodium acetate) with hydroxylamine salts. The reaction is carried out under N_2 and within 2 h, large clumps of acicular goethite, radiating from a central point, are formed (Ardizzone and Formaro, 1985).
5. Aeration of Fe^{II} oxalate solution in presence of NaOH ($\text{OH/Fe} = 2$) for 1–2 weeks at room temperature (Atkinson, 1976).
6. Conversion of lepidocrocite in M KOH at 70 °C over a 24 h period (Schwertmann and Taylor, 1972a).
7. Heating 0.1 M $\text{Fe(NO}_3)_3$ solution at 70 °C for 48 hr. Owing to the very low pH, the yield is only ca. 20% (Cornell, unpublished).

8. Conversion of ferrihydrite precipitated at pH 8 and buffered at pH 8.5 with 0.05 M NaHCO_3 in the presence of cysteine (cysteine: Fe = 1.1) at 70 °C for 60 hr. Addition of cysteine causes instantaneous darkening of the ferrihydrite and formation of a crystalline intermediate with an XRD pattern characterised by basal reflections at 1.04 and 0.504 nm. This intermediate transforms into a yellow precipitate of fairly monodispersed crystals (<100 nm across) of goethite (Cornell et al., 1991).
9. Storage of 0.7 M $\text{Fe}(\text{NO}_3)_3$ solution at an OH/Fe = 2 (pH 1.3–1.7) for 51 d at RT. A low yield of small acicular crystals ca. $24 \times 12 \times 4$ nm in size results (Morup et al., 1983; Glasauer, 1995).
10. Ageing of a partially neutralized $\text{Fe}(\text{NO}_3)_3$ solution at RT followed by transformation of hydrolysis products at pH ~12 and 62 °C (Atkinson et al., 1968).
11. Oxidation at 50 °C of Fe^{II} sulphate solution containing iron wire and lepidocrocite seeds (Nitschmann, 1938).

20.2.2

Lepidocrocite

Precipitate a 0.06 M FeCl_2 solution to pH 7 with NaOH and oxidize with air at a rate of 200 mL min^{-1} . Maintain the pH at 7 by addition of further NaOH. The reaction is carried out at room temperature with stirring and is complete within 3 h. Wash and dry the precipitate. The yield is ca. 6 g of thin, lathlike crystals.

Other methods

1. Precipitation of $\text{Fe}(\text{OH})_2$ from FeCl_2 solution with 2 M hexamethylenetetramine (urotropin) followed by oxidation for 3 h at 60 °C with a mixture of M NaNO_2 and HCl (Brauer, 1982).
2. Precipitation of green rust from an FeCl_2 solution at pH 7.5 with NH_4HCO_3 followed by oxidation with air at 50 °C at pH > 6.5 for ca. 8 h. This method gives well developed lath-like crystals (Giovannoli and Brüttsch, 1974).

20.2.3

Akaganéite

Hold 2 L of 0.1 M FeCl_3 solution in a closed vessel at 70 °C for 48 h. During this period the pH of the system drops from ca. 1.7 to 1.2 and a compact yellow precipitate forms. This method gives around 5 g akaganéite consisting of somatoidal crystals. The presence of Cl is essential.

Other methods

1. Storage of an FeCl_3 solution at pH 3 and 70 °C for several days after pre-ageing at an OH/Fe of 0.75 at RT for 48 h. This method gives rod-like crystals (Paterson and Tait, 1977).
2. Oxidative hydrolysis of FeCl_2 solution (Kiyama et al., 1972).

3. Hydrolysis of solid $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ by storage in contact with moist air for several months. The akaganéite crystals are separated from the remaining precursor by washing with bidistilled water (Pollard et al., 1992).
4. Hydrolysis of a 0.1 M FeCl_2 solution with urea at 100°C for 15 h (Ishikawa and Inouye, 1972).
5. Boiling of an FeCl_2 solution for ca. 10 min in the presence of dihydroxyethylene glycol. It is claimed that this gives large hexagonal crystals of akaganéite (Nightingale and Benck, 1960). Reeves and Mann (1991) have noted that suitable organic compounds can induce formation of limited amounts of akaganéite.

20.2.4

Schwertmannite

Preheat 2 L of distilled water to 60°C in an oven, quickly add 10.8 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3 g of Na_2SO_4 ($1000 \text{ mg SO}_4 \text{ L}^{-1}$) and keep the solution for further 12 min at 60°C . After cooling to room temperature, dialyse the suspension for a period of several days and finally freeze-dry the solid (Bigham et al., 1990).

Another route to schwertmannite involves bacterial oxidation with *Thiobacillus ferrooxidans* of an FeSO_4 solution at pH 2–3 (Bigham et al., 1990).

20.2.5

Feroxyhyte

Titrate 300 mL 0.1 M FeCl_2 solution to pH 8 with 5 M NaOH with stirring. Add 40 mL 30% H_2O_2 in one lot. As the reaction is violent, it should be carried out in a 2 L beaker in a fume hood. Upon addition of the oxidizing agent, the green suspension rapidly turns reddish brown. Centrifuge, wash and dry the product at 40°C . This method yields ca. 2.5 g feroxyhyte.

20.2.6

Ferrihydrite

2-line ferrihydrite

Add, with stirring, 330 mL 1 M KOH to 500 mL 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution to bring the pH to 7–8; the last few mL of alkali should be added dropwise in order not to exceed this pH. Centrifuge the suspension, then dialyse as rapidly as possible to remove all electrolytes and freeze dry the product. This method gives around 10 g 2-line ferrihydrite.

6-line ferrihydrite

Preheat 2 L of distilled water to 75°C in an oven, then add 20 g unhydrolyzed crystals of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with rapid stirring. Return to the oven and leave there for 10–12 min. During this time the solution changes from gold to dark reddish brown indicating the formation of Fe hydroxy-polymers. No precipitate should form. Cool rapidly by plunging into ice water, transfer to a dialysis bag and dialyse for at least

three days, changing the water several times each day. Then freeze-dry the suspension. This method gives around 5 g ferrihydrite (see Towe and Bradley, 1967).

Other methods

1. Thermal decomposition of iron pentacarbonyl; **NB** this is poisonous.
2. Rapid oxidation of FeCl_2 solution at pH 5 (Karim, 1984).
3. A full range of ferrihydrites varying in crystallinity and with between 2 and 6 XRD lines (Schwertmann et al., 1999) may be produced by:
 - a) Titrating a 0.1 M $\text{Fe(NO}_3)_3$ solution up to pH 7 with NaOH at a rate of between $10^{-3} - 10^{-1}$ mmol Fe min^{-1} at RT.
 - b) Oxidizing a 0.1 M FeCl_2 solution with air at RT and pH 6.5 and compensating for the H^+ production by adding NaOH solution containing increasing levels of Si (0.25–2 mg/ml).

20.2.7

Hematite

Preheat 2 L of 0.002 M HCl to 98 °C and then add 16.6 g $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to give a 0.02 M solution. Heat the solution at 98 °C for 7 d. A compact, bright red precipitate forms. Centrifuge, wash and dry the precipitate. This method gives ca. 3 g of fairly uniform, rhombohedral crystals.

Variations of this type of forced hydrolysis of acid Fe^{III} solutions at a temperature close to 100 °C involve different anions (Cl^- , ClO_4^-) and acidities (Matijevic and Scheiner, 1978; Penners and Koopal, 1986; Schwertmann and Cornell, 2000). Hematite seeds can be added and grown up to give bigger particles (Penners, 1985). Unusual morphologies may be produced using mixed solvents – water/ethanol or water/ethylene glycol (Hamada and Matijevic, 1982; Matijevic and Cimas, 1987).

Other methods

1. Hydrothermal transformation of ferrihydrite in a teflon bomb at 180 °C for several days yields platy crystals up to several μm in size (Schwertmann and Cornell, 2000).
2. Decomposition of iron chelates (e.g. Fe-EDTA or a solution of Fe^{III} salt in the presence of triethanol amine) in alkaline media (pH > 12) in an autoclave for one hour (Sapieszko and Matijevic, 1980).
3. Heating at 300 °C in air a mixture of $\text{Fe(NO}_3)_3$ and ethylene glycol (da Costa et al., 1994b).
4. Dehydroxylation of goethite or any other Fe oxyhydroxide at temperatures greater than 250 °C (Brown, 1980) or by dry grinding at RT (Mendelovici et al., 1982).
5. Oxidation of magnetite above 400 °C (Feitknecht and Mannweiler, 1967).
6. Transformation of ferrihydrite at pH 7–8 in the presence of NaHCO_3 buffer (Schwertmann and Cornell, 2000).
7. Oxidation of iron film in air at 1027 °C for 10 h (Gleitner et al., 1991).
8. Oxidation of iron powder held in 5–15 M NaOH solution at temperatures greater than 200 °C at 5 MPa of oxygen partial pressure (Uchida et al., 1993). Hematite

forms as micaceous plates, the diameter of which ranges from 5–45 μm depending on the NaOH concentration and the temperature.

9. Hydrothermal conversion of either ferrihydrite or goethite at 250–300 °C in alkaline media for some hours, followed by a further stage of growth at higher pH (Ostertag, 1994). Micaceous plates of hematite result.

10. Large crystals are obtained by heating Fe^{II} oxinate (or Fe-Al oxinate for Al-substituted hematite) at 700 °C (da Costa et al., 2001).

11. The *Gel-Sol* method of Sugimoto et al. (1993) involves ageing a highly, condensed ferrihydrite gel (1M and $\text{OH}/\text{Fe} = 2.7$) at 100 °C for eight days: the yield is close to 100%. Different crystal shapes are obtained by the use of different additives.

12. Thermal decomposition of Fe citrate in a crucible at 600 °C for 16 hr to produce large, platy crystals (G. Roach, priv. comm.).

13. Single crystals from 50–800 μm across can be synthesised by chemical vapour transport. Hematite powder is held for one week in a silica tube with a temperature gradient of 1000–850 °C in an atmosphere of $\text{HCl}(5.3\text{kPa})/\text{O}_2$ (133 Pa) (Moukassi et al., 1984).

14. Rapid oxidation of polished samples of iron in an air/acetylene flame produces a hematite coating of 50–100 μm in thickness for use as a hematite electrode (Curran and Gissler, 1979).

15. Doped hematite electrodes are produced by mixing hematite (99.998 purity) with TiO_2 or SnO_2 of the same purity, in acetone, evaporating the mixture at room temperature and compressing 0.5 g of the hematite powder in a die at 20–34 MPa; the resulting pellet is sintered at 1350 °C for 5–6 hr (Balko and Clarkson, 2001).

16. *Thin films* of hematite are grown on silicon wafers by ion beam induced, chemical vapour deposition (IBICVD). FeCO_3 vapour is passed over the silicon substrate which is bombarded by O_2^+ ions which decompose the iron compound (Yubero et al., 2000). The films are particularly suitable for optical and magneto-optical applications.

20.2.7.1 Coated Hematite

Coated particles are of interest for investigations involving catalysis, medicine and pigment production. The coatings which can be used to modify the properties of the underlying Fe oxide, may consist of a continuous, uniform shell around the core particle, or may be made up of very small particles that adhere to the core.

Hematite ellipsoids coated with an $\text{Sn}(\text{OH})_2$ shell were prepared by heating an aqueous dispersion of hematite (0.3 g L^{-1}) with 4.10^{-3} M $\text{Sn}(\text{SO}_4)_2$, 1.85 M urea and 0.31 M HCl at 80 °C for up to one hr; both continuous stirring during precipitation and careful control of the ratio of reactants/solid were essential to ensure that coated particles rather than a mixture of coated hematite and precipitated $\text{Sn}(\text{OH})_2$, were obtained (ul Haq and Matijevic, 1998).

Hematite coated with particles of $\text{Mn}(\text{OH})_2$ was prepared by heating an aqueous dispersion of hematite and $\text{Mn}^{\text{II}}2\text{--}4$ pentanedionate at pH 7.6 and 50 °C for 2.5 hr. The coating was converted to Mn_2O_3 by heating the sample in air at 750 °C (ul Haq and Matijevic, 1997). Hematite has also been coated with SiO_2 (Ohmori and Matijevic, 1992), Al_2O_3 (Kratovichl and Matijevic, 1987), *yttrium oxide* (Aitken and Matijevic, 1987), *Cr hydroxide* (Garg and Matijevic, 1988) and *zirconium oxide* (Garg and Matije-

vic, 1988a). The red emitting phosphor, $\text{Y}_2\text{O}_3\text{S Eu}^{3+}$ has been coated with a layer of hematite nanoparticles by first depositing magnetite particles on the phosphor and then heating them at 450°C to convert them to hematite (Merikhi and Feldman, 2000).

20.2.8

$\epsilon\text{-Fe}_2\text{O}_3$

1. Boil an alkaline solution of potassium Fe^{III} -cyanide and sodium hypochlorite and heat the resulting precipitate at 400°C ; pure, disordered $\epsilon\text{-Fe}_2\text{O}_3$ results (Trautmann and Forestier, 1965).

2. An $\text{Fe}_2\text{O}_3\text{-SiO}_2$ composite was obtained by heating nanoparticles of maghemite, well dispersed in silica ($\text{Fe}/\text{Si} = 0.7$) under an oxygen flux to 1400°C , holding them at this temperature for 30 min. and then cooling at a controlled rate to room temperature: more than 80% of the Fe oxide is in the $\epsilon\text{-Fe}_2\text{O}_3$ form (ordered material) with the remainder as hematite (Tronc et al., 1998). Formation of some $\epsilon\text{-Fe}_2\text{O}_3$ occurred when Si containing ferrihydrite ($\text{Si}/(\text{Si} + \text{Fe}) = 0.134$) was heated to $700\text{--}800^\circ\text{C}$ (Campell et al., 2002).

20.2.9

Magnetite

Bring a solution of 0.3 M Fe^{II} sulphate (560 mL) to 90°C and add 240 mL of a solution 3.33 M in KOH and 0.27 M in KNO_3 dropwise over a few minutes. Heat the suspension for 60 min with stirring, cool, wash and dry the black precipitate. It is essential that the entire preparation be carried out under an atmosphere of N_2 and that all solutions be outgassed with N_2 before use (David and Welch, 1956). To avoid any formation of Fe^{III} oxides either hydrazine or metallic Fe can be added (Regazzoni et al., 1981).

Other methods

1. Alkaline hydrolysis of Fe^{II} sulphate solution to give $\text{Fe}(\text{OH})_2$ followed by heating the product at ca. 100°C (Schikorr reaction, Schikorr, 1929), i.e.

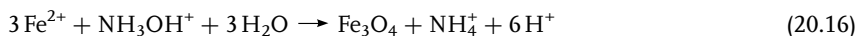


The whole reaction must be carried out under N_2 . This reaction can display complicating side effects (Regazzoni et al., 1981).

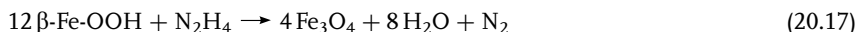
2. Reduction of hematite at 400°C in an atmosphere of 5% H_2 /95% Ar, saturated with water vapour and free from oxygen (Regazzoni et al., 1981).

3. Reaction of a 2:1 $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ solution, under alkaline conditions at 80°C under N_2 (Regazzoni et al., 1981).

4. Reaction at 85°C of Fe^{II} ammonium sulphate solution (buffered to pH 7–8 with sodium acetate) with hydroxylamine sulphate; the suspension is held under N_2 (Ar-dizzone et al., 1983) i.e.



5. Reductive transformation in a sealed ampoule of an akaganéite suspension in the presence of hydrazine at pH 9.5–11.5 and 100 °C (Blesa et al., 1986a):



6. Decomposition of an alkaline (0.2–0.4 M OH[−]) solution of Fe^{III}NTA (NTA/Fe = 1) at 217 °C in an autoclave (Booy and Swaddle, 1978). This method gives well formed octahedra, 10–100 μm in diameter.

7. Heating of iron hydroxide acetate at 200–260 °C under N₂ (Pinheiro et al., 1987).

8. Stable, nanometre magnetite particles form by boiling a mixture of Fe^{II} sulphate and bispyridoxylidene hydrazine phthalazine for 10 min. at pH 7 (Sarel et al., 1989).

9. Thermal decomposition of Fe^{II} sulphide in air at 500 °C (Robl, 1958);



10. Holding a solution of Fe^{III} acetylacetonate in 1-propanol under N₂ in an autoclave at 300 °C for several hr gives plates 9–11 nm across (Kominami et al., 1999).

11. Holding a very dilute suspension of magnetite particles in sodium silicate solution at room temperature for 4 days produces magnetite with a uniform, 3 nm SiO₂ coating (Philipse et al., 1994; Correa-Duarte et al., 1998).

12. Pure, crystalline, *thin films* of magnetite (111) can be grown on Al₂O₃ (001) or MgO(0001) substrates by oxygen plasma assisted, molecular beam epitaxy; the substrate temperature should not exceed 250 °C in order to avoid interfacial reactions and diffusion of Mg in the magnetite structure (Kim et al., 1997).

Magnetic paper was prepared by adding M^{II}(= Fe^{II} and Co^{II}) chloride solution to a dispersion of paper pulp followed by addition of NaOH to precipitate M(OH)₂. The metal oxide particles were forced into the internal cavities of the fibres by vigorous stirring during which oxidation to a ferrite, Co_xFe_{3-x}O₄ (0 < x < 1) took place. The product was well washed and paper formed by drying the pulp in a heated press (Carrazana-Garcia et al., 1997).

20.2.10

Maghemite

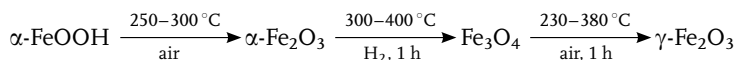
Heat synthetic lepidocrocite or magnetite in air (in a furnace) at 250 °C for 2 hr or 5 hr, respectively. The product will have the morphology of the precursor.

Other methods

1. Slow oxidation of a mixed Fe^{II}/Fe^{III} solution at RT and pH 7 (Taylor and Schwertmann, 1974a).

2. Oxidation of an Fe^{II} salt solution with air, urotropin, sodium iodate or sodium nitrate or with air in the presence of a complexing agent such as pyridine or sodium thiosulphate (Robl, 1958).

3. Heating of goethite or ferrihydrite in air at 450 °C for 2 h in the presence of an organic material such as sucrose (Schwertmann and Fechter, 1984).
4. Thermal decomposition of FeOOCH_3 at 290 °C in vacuo (Kikkawa et al., 1976).
5. Multi-stage transformation from goethite, i.e.



(Maeda, 1978).

6. Vapour decomposition of FeCl_3 in an oxygen/hydrogen flame (Batis-Landoulis and Vergnon, 1983).
7. Thermal decomposition of Fe^{II} malate or other Fe^{II} organic salts (Nikumbh et al., 1993) and Fe^{II} and Fe^{III} oxalate (Music et al., 1994).
8. Electrolysis of Fe^{III} nitrate solution (Davey and Scott, 1957).
9. Heating a mixture of $\text{Fe}(\text{NO}_3)_3$ and ethylene glycol at 300 °C under N_2 (da Costa et al., 1994b).

20.2.11

$\text{Fe}(\text{OH})_2$

Mix Fe^{II} sulphate solution with NaOH solution to give a pH of 8 and age with stirring at 70 °C for 7 h in an atmosphere of N_2 . The white precipitate is filtered and dried under vacuum. It is essential that all solutions are thoroughly freed from oxygen (e.g. by passing through an alkaline pyrogallol solution) and that the entire preparation be carried out in the absence of oxygen – either in a glove box or a Schlenck apparatus (Miyamoto, 1976).

Other methods

Precipitation from Fe^{II} hexaminehydroxide solution by evaporation of NH_3 ; all carried out under N_2 (Feitknecht et al., 1969).

20.2.12

Green rust

Titrate 0.1 M Fe^{II} sulphate or chloride solution with M NaOH in a closed system and under N_2 to pH 6.5–7 and then, while maintaining the pH by addition of M NaOH , slowly oxidize with a stream of CO_2 -free air. Upon formation of a green precipitate (partial oxidation), separate this precipitate, still keeping it under N_2 and freeze dry it (Schwertmann and Fechter, 1994; Lewis, 1997; Refait et al., 1999). The preparation of a carbonate green rust is described by Taylor (1982) and Génin et al. (1998).

20.2.13

Other compounds**FeO (nonstoichiometric)**

Mix iron and hematite powder, pelletize the mixture and heat to 837 °C in a sealed silica or gold tube for 24 h. After heating, quench in liquid N₂ (Battle and Cheetham, 1979).

Another method is to reduce hematite powder with H₂/H₂O at 800 °C followed by annealing for 2 weeks in the presence of FeCl₂ (to assist recrystallization): this produces Fe_{0.94}O (Moukassi et al., 1984). Doping with Mg, Ca or Mn is achieved by reduction of a mixture of hematite powder and the carbonate of the doping ion.

High pressure FeOOH

Hold hematite powder in KOH solution at 400 °C and under a pressure of 8 GPa in an autoclave for one hour (Pernet et al., 1973).

20.2.14

Production of iron oxides on substrates or in confined spaces**Goethite, hematite and ferrihydrite**

A patterned array of goethite can be deposited from an Fe(NO₃)₃ solution at 70 °C on an organic substrate mounted on a silicon wafer (Rieke et al., 1994). The organic surface contains a mixture of sulphonate groups (which bind the iron oxide) and non-binding methyl groups (which permit development of a pattern).

Nanometre hematite is produced by impregnating SiO₂ powder (with and appropriate pore size) with Fe(NO₃)₃ solution, filtering the powder and heating at 600 °C for 3 hr (Morris et al., 1989).

A method of coating SiO₂ sand grains with various Fe oxides for use in percolation experiments, was developed by Scheidegger et al. (1993) (cf. Schwertmann and Cornell, 2000).

Ferrihydrite can be precipitated from the pores (< 8 nm) in chrysotile by impregnating the pores with FeSO₄ solution and holding the solid in M NaOH at 30 °C for 15 hr (Ozeki et al., 1994).

Ferrihydrite can be photodeposited onto vycor glass by vapour deposition of Fe(CO)₅ solution followed by irradiation with UV light (Mendoza et al., 1991).

Magnetite

A self assembled monolayer of magnetite particles on a silicon wafer can be prepared by coating the silicon with polydimethyl-diallyl ammonium chloride (PDDA), irradiating the wafer in a microwave oven and then dipping the wafer for at least 5 min in an aqueous suspension of magnetite particles followed by washing the whole in distilled water. The microwave treatment reduces the surface roughness of the organic layer and promotes better ordering of the magnetite particles (Correa-Duarte et al., 1998). Multilayer films are prepared by the layer-by-layer (LBL) self assembly method in which the PDDA coated wafer is dipped into a suspension of mag-

netite or SiO₂-coated magnetite, washed and the whole procedure repeated up to ten times (Aliev et al., 1999). These magnetite films can also be prepared on exfoliated montmorillonite particles in which case, the individual layers in the film can be distinguished (Mamedov et al., 2000). Multilayers of magnetite particles have been deposited on polystyrene latex particles that had been coated with a polyelectrolyte film; the coated latex particles were mixed with the stabilised magnetite for ca. 20 min, filtered and washed, after which, a further layer of polyelectrolyte film was deposited and the whole process repeated until the required number of layers had been built up (Caruso et al., 1999).

Boron nitride capsules containing 10–20 nm particles of magnetite were produced by forming pellets of boron nitride; magnetite in a ratio of 8:2 and arc melting the pellets in an Ar/N₂ atmosphere for a few minutes. HRTEM confirmed that the magnetite particles were encapsulated in the boron nitride (Hirano et al., 1999).

Magnetite impregnated polymer gels (“elastic magnets”) were prepared by holding 100 nm slices of gel in 0.2 M FeCl₂ solution at room temperature under N₂ for two days; the gel was then washed and held overnight in M NaOH. XRD and magnetization experiments indicated that the gel had been mineralized with magnetite (Breulmann et al., 1998).

Precipitation of goethite, ferrihydrite or magnetite in vesicles

These oxides have been precipitated in unilamellar phosphatidylcholine vesicles (30 nm diameter) during studies of biomineralization of iron oxides (Mann and Hannington, 1988). Vesicles containing Fe^{II}, Fe^{III} or Fe^{II}/Fe^{III} solutions are prepared by ultrasonication of the appropriate Fe solution containing a lipid film, the excess Fe solution removed by passing through a cation exchange column and the iron oxide precipitated inside the vesicles by addition of aqueous NH₃ or NaOH. The suspension is held at 4 °C in the dark for 8–10 days after which time a crystalline precipitate can be identified by electron diffraction.

21

Environmental significance

21.1

Introduction

Over the last decade iron oxides have been recognized as being solid phases which exert a significant effect on the behaviour of a large range of environmentally relevant substances particularly heavy metals and other toxic elements, eutrophication compounds, and organic xenobiotics. Nowadays, these substances are inevitable constituents of most compartments of the earth's ecosystems, especially in densely populated and highly industrialized regions and also in those which practise intensive agriculture. Iron oxides indirectly affect the environment by influencing the fate (mobility, decomposition) of the substances listed above. Owing to their generally high affinity towards such compounds, Fe oxides can deactivate pollutants by surface adsorption or by incorporation. These deactivation processes operate in the ecosystem and are also used extensively in environmental technologies such as water purification and incineration of waste materials. Since, however, Fe oxides may dissolve under anoxic conditions, the hazardous chemicals may again be released back into the environment. Release may also take place spontaneously (ageing) or during the heating process used to reduce the volume of the waste material, which turn Fe oxides into less active forms (ferrihydrite to hematite). Fe oxide surfaces show catalytic activity in connection with the detoxification of organic xenobiotics.

This general situation has led to a burst of research activities into the role Fe oxides play in environmental management practices. The results have, in turn, widened our basic understanding of the nature and properties of Fe oxides. Some overlap between this chapter and almost every other chapter in the book is, therefore, unavoidable, but will be kept to a minimum by cross references.

21.2

Retention of pollutants by Fe oxides in water purification and in natural systems

21.2.1

Water treatment systems

Owing to their high surface area and affinity for ions and molecules, *poorly crystalline iron oxides* (mainly akaganéite and ferrihydrite) can be used in *water treatment plants* to adsorb unwanted elements and ions (Matthes, 1981; Benjamin et al. 1982; Pierce & Moore, 1982; Koppers, 1985; Mark et al. 1988; Singh et al. 1988; Appleton et al. 1989; Nakazawa et al. 1989; Carpenter et al. 1990; Manzione et al. 1990; Deininger & Merkl, 1991). The common method of doing this is to raise the pH of the waste water with $\text{Ca}(\text{OH})_2$ solution after adding Fe^{III} chloride; the Fe oxide that precipitates (probably 2-line ferrihydrite) binds essentially all the heavy metals. The precipitate is then filtered off and is usually dumped in storage valleys or pits.

In recent years there has been an increase in studies in which the potential of Fe oxides to remove various pollutants has been evaluated. A key problem when using an Fe oxide filter is to establish good hydraulic conditions in the filter and to maintain sufficient physical stability. Freeze-drying was used to produce a granular Fe oxide consisting of poorly crystalline akaganéite for arsenate removal from water (threshold concentration $10 \mu\text{g/L}$) following oxidation of As^{III} to As^{V} by Mn^{IV} oxide (Driehaus, 1994). Upon storing As-containing Fe oxide sludge in a closed container, soluble As^{V} increased first from 5 to $700 \mu\text{g/L}$ because of the reductive dissolution of Fe and then decreased because As^{V} is reduced to As^{III} and fixed by pyrite (Meng et al. 2001). Phosphate which also has a high affinity for the Fe oxide surface, competed with arsenate because of its much higher concentration in the water.

In a model experiment, in which arsenate and chromate solutions were passed through a column of Fe oxide coated sand (50 mg Fe/kg), the breakthrough was delayed against that of the blank by ca. 8 pore volumes for chromate and by ca. 30 pore volumes for arsenate (Martin and Kempton, 2000). ^{90}Sr could be successfully removed from Pu processing high-pH salt waters in the Hanford Nuclear Reservation, by percolating it through a column of Fe-oxide coated sand containing 2.1% Fe (Hansen et al. 2002). Adsorbed arsenate on ferrihydrite was fairly stable against reduction to the toxic As^{III} by a glucose fermenting organism (CN 8) which, however, readily reduced dissolved arsenate (Langner and Inskeep, 2000). Arsenate may, however, be partially released when ferrihydrite turns into goethite/hematite on ageing (Ford, 2002). Morrison et al. (1995) investigated the adsorption of U^{VI} on ferrihydrite and coupled the data with a reaction/transport model for contaminated groundwater which included economic factors.

Natural Fe oxides have also been used for water purification. In a laboratory study, a natural ferrihydrite (surface area of $243 \text{ m}^2 \text{ g}^{-1}$) originating from a ferriferrous acid spring turned out to be capable of removing $>95\%$ of the inorganic phosphate from water with 0.1 mg P L^{-1} (Weiß et al., 1992). The so-called Red Mud, a waste product of the alumina industry, containing 330 g Fe/kg was also effective, whereas a tropical soil with $80 \text{ g kg}^{-1}\text{Fe}$ was comparatively less so (Weiß et al., 1992a). Nine

different Fe-oxide-rich sludges with 280 to 500 g kg⁻¹ Fe present as 2-line ferrihydrite produced by deferration of drinking water successfully removed phosphate from sewage water (Thole et al., 1992). The sludges replaced Fe^{III} salts commonly used for this process, but removed only one tenth as much P per Fe as these salts. As laboratory experiments predicted (see Chap. 11) P elimination (i.e. adsorption on the sludge) decreased strongly with increasing pH.

A second procedure in which an Fe compound is used to clean sewage is to add powdered *magnetite* (Dayton, 1993), which is positively charged at acid pH, to the sewage where it attracts negatively charged organic particles. These magnetite-organic associations are quickly separated and removed from the sludge with the aid of large magnets and the organics are then desorbed under alkaline conditions. Anodically polarized magnetite has been investigated at nuclear fuel processing facilities as a possible means of extracting pertechnetate TcO₄⁻ from radioactive waste and reducing it to the less soluble TcO₂ (Farrell et al. 1999). Detoxification of chromate (Cr^{VI}) through reduction to Cr^{III} at the magnetite surface has also been reported (Peterson et al. 1996).

Zinc was immobilized during the anoxic reduction of goethite by *Shewanella putrefaciens* either by incorporation into siderite, FeCO₃, or into a better crystalline goethite. Reduction of lepidocrocite to magnetite had the same effect. Nitrate being a preferred electron acceptor inhibited both these incorporation pathways (Cooper et al. 2000). Magnetite is also used to remove metals by a cation exchange procedure. In this process, a magnetic metal-binding polymer (e.g. a cation exchange resin) is first created by oxidizing adsorbed Fe²⁺ at pH 10 and 60–70 °C to form magnetite. This composite is mixed with the polluted material, then separated with a ferromagnetic wire and finally regenerated by desorbing the metals (Leun and Sengupta, 2000). Various heavy metal ions have been removed from waste water by aerial oxidation of Fe(OH)₂ suspensions (slightly alkaline pH; 65 °C) to form metal-substituted magnetite. This so-called ferrite process is used in Japan with the magnetite being separated from the liquid magnetically (Tamaura et al. 1979).

A third method used for remediation of polluted waters and aquifers involves *metallic iron*, Fe⁰. This rather expensive process is used for removal of chlorinated organics, such as CCl₄, detoxification of chromate by reduction to Cr^{III} and adsorption of UO₂²⁺. The system normally consists either of a perforated barrier of iron metal or of iron filings or wires mixed in a percolation column. Interaction of the pollutants takes place at the surface of corrosion products, i.e. the Fe^{II}- and Fe^{III}-phases. Most of these experiments are at the pilot plant stage. Among the corrosion products identified are green rusts, magnetite, maghemite and siderite and the pollutants interact with these phases. After percolation for 5 months with a neutral sulphate or bicarbonate solution which had first passed through a microbially active sludge, goethite, lepidocrocite, akaganéite, magnetite/maghemite, and green rusts were formed (Gu et al. 1999; Mantha et al. 2001). The oxides may exert a range of effects on the system: i.e. they may function as adsorbents/occludants for the toxic species and as catalysts, but they may also block the metal surface thereby hindering further chemical reactions. In the latter case, they can be removed with acid to reactivate the surface (Mantha et al. 2001).

In a sand column with iron filings (150 μm size) which was used for immobilizing chromate in fly ash, the Cr concentration was reduced from 25mg/L to below the detection limit (0.0025mg/L); the Cr was associated with the Fe oxides, probably ferrihydrite and precipitated as Cr oxide or as Ca chromate (Astrup et al. 2000). Goethite and akaganéite together with siderite and FeS were identified in a barrier of Fe filings 0.5mm thick and 3–24 mm long, installed to remove U from the contaminated groundwater at the Y-12 plant site at Oak Ridge (Phillips et al. 2000). An EXAFS study of the corroded material after percolation of an arsenate solution through iron wire, found As-Fe interatomic distances of 0.324–0.329 and 0.344–0.345 nm indicating bidentate, corner sharing between AsO_4 tetrahedra and FeO_6 octahedra. These were different from those in scorodite, FeAsO_4 , but typical of arsenate adsorbed on an Fe oxide (possibly magnetite or maghemite). The As was not reduced (Farrel et al. 2001). Jacobi and v.Reichenbach (pers. communication, 1994) used a mixture of granules of clay, cement, powdered iron metal and some aluminium, all crushed to form porous particles. One ton of granules took up 130 kg of heavy metals. The process continued until all the iron was converted to iron oxide. The high concentration of heavy metals in the iron oxide makes their re-extraction economically feasible. This process was more economical than the usual precipitation/filtration procedure.

21.2.2

Natural systems

Whenever Fe oxides, especially ferrihydrite, are formed in nature, a range of toxic or unwanted elements is coprecipitated. A case of natural detoxification of arsenic by Fe oxides was observed on the Coral Reef of Amberlite Island, Papua New Guinea. Upon reaching the aerobic surface waters, hydrothermal fluids rich in dissolved As and Fe, lose their As (and Fe) almost completely by adsorption on and/or coprecipitation of 2-line ferrihydrite. The precipitate contained (besides tens of mg of Cu, Pb, Zn) 55g/kg As, and, thus, it prevented any damage to the biota (Pichler & Veizer, 1999). Arsenic peaks (0.1–0.6 μM) at a depth of 2–6 cm in surficial sediments in 16 Canadian lakes were closely correlated with hydroxylamine reducible Fe (0.2–1 mM), suggesting again a close association between As and poorly ordered Fe oxides (Belzile & Tessier, 1990).

As-containing Fe-oxide-rich particles from 12 lakes in the Canadian Shield had As/Fe mole ratios between 0.07 and 0.007, with all As being pentavalent. Complementary laboratory experiments indicated that adsorbed As^{III} is readily oxidized to As^{V} and that the field-derived equilibrium parameters for adsorbed arsenate are essentially identical to those found for ferrihydrite in the laboratory (DeVitre et al. 1991). Iron oxides, probably ferrihydrite, precipitated biotically in an abandoned underground Fe ore mine by the species *Leptothrix* and *Gallionella* (see Fig 17.8) strongly adsorbed Sr, Cs, Pb and U. The distribution coefficients were in the range $10^{3.0}$ to $10^{4.7}$ ($\text{Sr} < \text{U} < \text{Cs} < \text{Pb}$). They decreased as the easily reducible (by hydroxylamine) amount of the Fe oxide increased, probably due to increasing competition from bacterially produced organic compounds which shielded the oxide surface (Ferris et al. 2000). On the other hand, biogenic reduction of the mobile uranyl (U^{VI}) to

the relatively insoluble U^{IV} may be hindered by Fe oxides because the latter are reduced in preference to U (Wielinga et al. 2000).

Radioactive cobalt (^{60}Co) may be mobilized in the environment by the commonly used and omnipresent complexing ligand EDTA. In a model experiment with a goethitic pleistocene sediment and with pure goethite, the Co of a $Co^{II}EDTA$ complex was replaced, under anoxic conditions, by microbially produced Fe^{2+} and subsequently immobilized by adsorption on the goethite (Zachara et al. 2000). Cobalt in Co^{III} -substituted goethite ($Co_{0.01}Fe_{0.99}OOH$) was bio-reduced under strictly anaerobic conditions by *Shewanella putrefaciens* to Co^{2+} which was then strongly adsorbed by the remaining goethite (Zachara et al. 2001). 5 mol% Ni in a ferrihydrite coprecipitate retarded the bioreduction of the ferrihydrite by some as yet, unknown mechanism (Fredrickson et al. 1998; 2001).

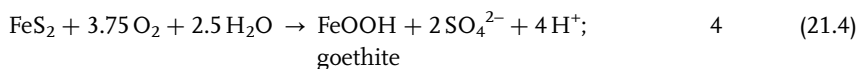
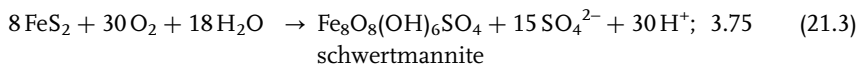
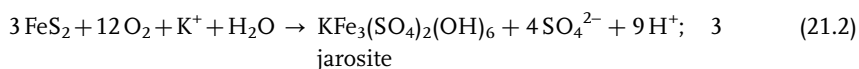
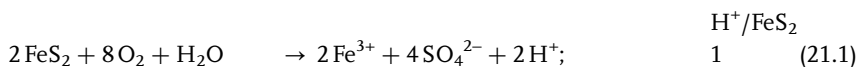
Based on a significant positive correlation between oxalate extractable Fe and the P adsorption coefficient in the recent sediments in the North Sea (German Bight, Skagerak), ferrihydrite is considered to be the dominant young Fe oxide which regulates phosphate activity in this marine environment into which the streams from the surrounding countries have released significant amounts of phosphate (Slomp et al. 1996). Similarly, in 0.05–1.0 μm particles collected from streams in the Tualatin River Basin, Oregon, the concentrations of P (0.005–0.135 $mg\ L^{-1}$) and Fe (0.095–1.625 mg/L) were positively correlated ($r^2 = 0.83$; $P < 0.001$), suggesting their close association (Mayer & Jarrell, 1995). For decontamination of soils and aquifer material by a pump-and-treat technique, percolation with the cationic surfactant, hexadecyltrimethyl-ammonium bromide, (0.001 M) is suggested because this dispersed very selectively the small amount of goethite considered to retain the contaminants, without reducing permeability. Similar selective dispersion was achieved with 0.0005 M $CaCl_2$, pH 3.0 (Seaman and Bertsch, 2000).

21.3

Acid Mine Tailings

Drainage waters from pyrite (FeS_2)-containing ore and coal mining overburden are usually extremely acid due to the sulphuric acid formed by bacterial oxidation of pyrite and are therefore called acid mine drainage (AMD). Because pyrite is a scavenger of almost all toxic metals (Pb, Zn, Cu, Cd, As, Ni, Co etc.) AMDs are also often rich in these metals and are, therefore, a hazard to the ecosystem for two reasons, namely their high acidity and toxic element content (for a recent review see Nordstrom and Alpers, 1999). Thus, pyritic mining produces acid waters containing heavy metals and contaminated tailings which usually are not hospitable to revegetation. For example, in vivo studies of swine fed with tailings from the Leadville mining district of Colorado, have shown that Pb bioavailability was less than 5 % where Pb was still in galena (PbS) but up to 45 % of the total Pb in the Fe-Mn-Pb phases (Casteel et al. 1997).

The amount of acid produced by the oxidation of sulphides (mainly pyrites) and the type of Fe^{III} minerals formed are connected to the degree to which the Fe^{III} is hydrolysed (hydroxylated):



Because of their strongly acidic character the AMDs must be neutralized before entering the natural water system. This can be achieved either by bringing them into contact with those soils or rocks which often have a substantial acid neutralizing capacity (ANC), e.g. calcite and ankerite in the Core d'Alene Mining District (Balistieri et al. 1999), or by adding basic material, such as CaO ("quick lime"), Ca(OH)₂ ("hydrated lime") or CaCO₃ ("limestone"). Basic waste materials, such as sewage sludge or fly ash have also been proposed as neutralizing agents. Another and less costly procedure involves sedimentation basins, so-called wetlands in which AMDs are treated aerobically or anaerobically with compost-lined limestone drains to induce the precipitation of large amounts of Fe oxides. In such a system in the mining district of Ohio, the primary mineral formed was schwertmannite which gave place to goethite at an estimated rate of between 10 and 30 mol m⁻³ yr⁻¹ (Gagliano et al. 2003). Under acid and aerobic conditions this transformation follows eq (14.4; p. 385), whereas in the lower part of the column i.e. near organic waste, Fe is reduced and forms goethite on reoxidation.

As seen from the above equations, solid hydroxylated Fe^{III} compounds which are formed from the Fe sulphide provide the system with a high potential for the inactivation of toxic elements by coprecipitation and adsorption. The following examples illustrate the role Fe oxides play in regulating the behaviour of toxic elements in AMD systems. Arsenate released by oxidation of arsenian pyrite in the Mother Lode Gold district, California, was effectively adsorbed by the simultaneously precipitated goethite (Savage et al. 2000). The precipitation of Fe oxides (schwertmannite, ferrihydrite, goethite) along an alpine creek fed by a weathering pyritic gneiss reduced the As concentration drastically from >200 µg L⁻¹ at the source to <0.5 µg L⁻¹ ca 200 m away from the source. The Fe oxides accumulated up to 18 mg g⁻¹ As (Rüde et al. 2000). A goethite with 11% SO₄ was collected from AMD from a Pb-Zn mine in New Zealand which showed a pH₅₀ (i.e. the pH at which 50% of the metal is adsorbed; see chap. 11) about one pH unit lower than that of synthetic schwertmannite and 2-line ferrihydrite. This was attributed to a ternary complex Fe-O-SO₄-M (M = cation), since removal of SO₄ by Ba²⁺ or replacement of it by OH (i.e. at high pH) eliminated this difference (Webster et al. 1998). EXAFS spectra also suggested that ferrihydrite, and an "Al-Si-rich gel" were the preferred sinks for UO₂²⁺ in an uranium mine tailings in France (Allard et al. 1999). Best fits of EXAFS spectra also suggested that between 35 and 47% of the Pb in the tailings of the Leadville mining area in Colorado was associated with newly formed goethite (Ostergreen et al. 1999). In the

historic mining district at Butte, MT, liming facilitated the alteration of pyrite to ferrihydrite which, in turn, five years after the closing of the mine had sequestered weight percentages of As, Pb, Cu and Zn (Davis et al. 1999). A bacterial procedure for removing heavy metals from the AMD is being tested in the famous copper mine of Falu, Sweden, in a pilot plant. With mesophylic (35 °C) bacteria, an Fe concentration of 3.5 g L⁻¹, a pH of 1.8 and a flow rate of 330 L h⁻¹, an oxidation rate of 750 mg L⁻¹ h⁻¹ Fe was achieved (Sandström & Mattson, 2001).

The scavenging of Hg^{II} by suspended particles of iron oxide downstream from an unfiltered AMD from the abandoned New Idria HgS-mine, Calif., was found to be responsible for a drastic reduction of mobile Hg (e. g. from 12 to 0.6–0.8 µg L⁻¹ Hg) over a distance of 7.5 km along which the Fe (from pyrite) was precipitated, probably as schwertmannite ($K_d \sim 10^6$) (Ganguli et al. 2000). At the confluence of an AMD stream (Snake River, Colorado) and a pristine stream (Deer Creek), 40% of the dissolved organic matter was adsorbed by the Fe oxides precipitating at this point (McKnight et al. 1992). Sulphate, either adsorbed or bound in schwertmannite will be partly released into the liquid phase when it is transformed to goethite (Herbert, 1996; Rose and Elliott, 2000) whereas toxic elements, such as As and Cr, will probably be readsorbed by the goethite depending on pH (S. Regenspurg, pers. comm.). The acidophilic Fe^{III} reducer *Acidiphilium cryptum* JF-5 reductively dissolved pure schwertmannite and sulphate was released whereas arsenated and chromated schwertmannite was not reduced, and so remained inactivated, probably because of their biotoxicity (Regenspurg et al. 2002). A method for Fe removal as magnetite, recently proposed by Morgan et al. (2003), consists of oxidizing it at pH 10.5 in the presence of magnetite seeds.

It must be kept in mind, however, that once the tailings are exposed to anoxic conditions, as in so-called wetlands, the Fe oxides may be reductively dissolved and the capacity for retention of toxic elements is lost. This was shown in a laboratory study for arsenate and metal cations (Langner and Inskeep, 2000). The same took place in the pore water of a gold-tailing impoundment from a mine in Ontario where arsenic from arsenopyrite was the main pollutant. The hematite and maghemite produced in the roasting process retained the arsenic, but under anoxic conditions, chemolithotrophic bacteria reduced the Fe oxides, and so caused all the As (up to 100mg/L) to reappear in the aqueous phase. Lowering the redox potential further, immobilized the As, this time as a sulphide phase. Partial re-activation may also occur after heat treatment, as shown for an impoundment of acid tailings from a gold mine in which the arsenian Fe^{III} oxide hydroxide had been converted to hematite and maghemite (McCreadie et al. 2000).

21.4

Detoxification reactions

In the environment, Fe^{III} oxides may help detoxify pollutants through a range of redox reactions. Chromate (Cr^{VI}) is a toxic form of Cr, whereas Cr^{III} is not. Reduction of Cr^{VI} to Cr^{III} is, thus, a detoxifying process and takes place in soils and sediments

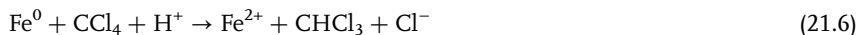
under anoxic conditions. In this process Fe^{II} may act as an electron donor with an Fe oxide being formed:



Upon adsorption of Fe^{2+} at a solid surface, the standard redox potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair is reduced substantially from 0.77 V to 0.35–0.45 V (Wehrli, 1990) thereby facilitating the electron transfer. Buerge and Hug (1999) have demonstrated that this higher reactivity may be responsible for the fact that solid phases (Fe oxides, SiO_2 , and clay minerals) in natural systems accelerate Cr reduction and that goethite and lepidocrocite are by far more active in this respect than the rest of the solid phases, because these two FeOOH forms adsorb much more Fe^{2+} . The authors attribute this to better overlap and charge delocalization at the surface of the Fe oxides.

Hexavalent Cr reacts with magnetite to form Cr^{III} . The reaction leads to a surficial transformation of magnetite into maghemite, and as seen from XANES and EXAFS spectra at the Cr-K edge, a rim about 1–2 nm thick around the magnetite crystal is formed which blocks further reaction (Peterson et al. 1997). XANES at the As K-edge and solution chemistry showed that As^{III} was increasingly oxidized to As^{V} in the presence of Mn-goethite as the Mn-for-Fe substitution increased from 0 to 10 mole%. O_2 rather than structural Mn^{III} appeared to be the final electron acceptor (Sun et al. 1999). Natural and synthetic ferrihydrite were found to be capable of detoxifying Sb^{III} by oxidizing it to the non toxic Sb^{V} in a first-order reaction (Belzile et al. 2001).

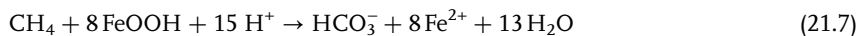
For detoxification of carbon tetrachloride (CCl_4), e.g. in groundwater, de-chlorination is necessary. Iron metal, Fe^0 , is commonly used for this purpose.



Reduction at the surface of Fe^0 is mediated by an oxide film which may consist of green rust, magnetite or maghemite and which supplies conduction band electrons; this reaction is intensified by light (Balko and Tratnyek, 1998). Species which are bound to the oxide, e.g. borate, strongly inhibited CCl_4 reduction by occupying the active sites (Johnson et al. 1998). The detailed mechanism of electron transfer through the oxide layer is discussed by Scherer et al. (1998). On the other hand, passivation of the Fe^0 surface by an oxide layer has also been observed. This could be overcome by the addition of the bacterium *Shewanella alga* which adheres to the Fe^0 barrier (Gerlach et al. 2000).

In a similar way, Fe^{2+} adsorbed on goethite, but not in the absence of goethite, promoted the dechlorination of CCl_4 to CHCl_3 at 30 °C. When the regeneration of Fe^{2+} took place, the reaction rate was first order with respect to the concentration of CCl_4 , second order with respect to the concentration Fe^{2+} and zero order with respect to H^+ concentration. The role of goethite is to fix the position of two Fe^{2+} ions at the oxide surface in a manner suitable for electron transfer to CCl_4 . Fe^{2+} produced bacterially (by *Shewanella*) from goethite was effective in the same way (Amonette et al.

2000). Methane produced in strongly anaerobic environments such as town refuse dumps is oxidized through reduction of Fe oxides, i. e.



21.5

Bacterial turnover of environmental pollutants

Organic pollutants often end up in natural and anthropogenic surface and subsurface environments. As long as the conditions there are aerobic, these pollutants may be readily oxidized by bacteria to CO_2 with O_2 as a final electron acceptor. However, high water saturation in the ecosystem creates an oxygen deficiency, thereby blocking oxidative detoxification. Fe oxides may then function as alternative electron acceptors. Heron et al. (1995) found that after percolation of organically polluted water for 15 years, the Fe oxides in a landfill were completely reduced. As^{V} , both that adsorbed and that coprecipitated with 2-line ferrihydrite was anaerobically reduced to As^{III} by *Sulfospirillum barnesii* together with some Fe^{III} from the ferrihydrite, but As reduction also took place without Fe reduction. The As^{III} formed was (re)adsorbed by the ferrihydrite (Zobrist et al. 2000). *Shewanella algae* reduced – and thereby detoxified – Cr^{VI} indirectly by a coupled biotic/abiotic pathway in the presence of hematite, goethite and 2-line ferrihydrite much more effectively than in the absence of these Fe oxides. The reduction was achieved through Fe^{2+} produced biotically at a rate of between 1.6 and 3.4 $\mu\text{g Cr}^{\text{VI}}/\text{mg-cells} \cdot \text{hr}$ (Wielinga et al. 2001). The role soil iron oxides play as an electron buffer in the bio-remediation of organic waste water was investigated in a model study with glucose-containing water. The amount of Fe^{2+} formed increased in proportion to the amount of glucose added (Ugwuegbu et al. 2001).

21.6

Anthropogenic dust and industrial sites

Ferrimagnetic phases (magnetite/maghemite) and hematite originating from all kinds of combustion processes and from steel production are common products in industrial and urban areas and are also widely dispersed in atmospheric dust. Ferrimagnetic phases can be easily identified by simple magnetic measurements, especially magnetic susceptibility, saturation magnetization and coercivity (see chap. 6 and 7). For example, at an abandoned shunting site in the Ruhr Area, Germany, the susceptibilities were significantly higher ($2.6\text{--}4.7 \cdot 10^{-5} \text{ m}^3 \text{ kg}^{-1}$) than in the nearby soils ($0.14 \cdot 10^{-5} \text{ m}^3 \text{ kg}^{-1}$) (Hiller, 2000).

The industrial dust deposited in the metropolitan area of Shanghai consisted of high-coercivity (hematite) and low-coercivity (magnetite/maghemite) particles, usually $< 10 \mu\text{m}$ in size. Four different dust sources could be distinguished on the basis of magnetic properties (Shu et al. 2000). Given previously reported links between

magnetic properties and mutagenicity in respirable particles, these results may help identify areas of risk to health. Goethite, substituted with 3 mol% Zn and Zn-substituted magnetite (by EXAFS) in a soil from an abandoned Zn smelter site in France were suggested as being effective sinks for Zn (Manceau et al. 2000). Two-line ferrihydrite identified by SAED in surface-weathered, 10 year-old, coal fly ash was found to retain higher concentrations (0.2–2% wt%) of Cr, Ni and Zn than did the associated silicate clay (Zevenbergen et al. 1999).

21.7

Iron-oxide rich waste products

Various well-known industrial and municipal waste products particularly those from the base metal industry, contain appreciable amounts of Fe oxides which may make them suitable for remediation purposes. Two examples from industry are the residues from the alumina and the titanium industries. The extraction of either Al or Ti from the natural ores (bauxite and ilmenite/rutile, respectively) leaves behind an alkaline and acidic (sulphuric) residue, respectively, in which Fe oxides are enriched, as indicated by their names “Red Mud” and “Red Gypsum”. A sample of *Red gypsum* is reported to contain ca. 35% of Fe oxide consisting of goethite and hematite, half of which was oxalate soluble (Fauziah et al., 1996). As expected, this material had an appreciable adsorption capacity for phosphate and heavy metals and, if added to soils, could confer these properties on them (Peacock & Rimmer, 2000),

Similar Fe oxide contents are found in *Red Muds*. Beneficial effects on crop yields were noticed especially for acid sandy soils (Australia; e.g. Summers et al. 1996, 1996a) and acid high-moor peat soils (Germany; Scheffer et al. 1986; 1991), both naturally being very low in Fe oxides. Their P-binding capacity was, thus, substantially raised so that the P-supply to crops improved without the disadvantage of P and fluoride leaching to the ground water. To reach this goal, application rates to the peat soil should remain below 10–20 t ha⁻¹, when no gypsum has to be applied, to avoid soil alkalinity. On the other hand, both the Cr and As content increased in the top horizon of the peat soil and, although neither elements moved into the subsoil, the application was stopped after 9 years. Goethite waste originating from the hydrometallurgical extraction of zinc ores (from a plant in Sardinia) can be recycled to form a glass-ceramic product for use in the construction industry: the goethite was mixed with granite and glass cullet waste, the mixture melted to form a glass and then heat-treated to produce glass ceramics (Pelino et al. 1997).

Other Fe-oxide enriched waste products are *sludges* from sewage treatment with Fe salts to eliminate phosphate (e.g. 500.000 t a⁻¹ in Germany). Because of their high phosphate content these sludges are applied to soils as a fertilizer. In a pot and field study with seven soils in Germany, the P concentration in the soil solution and P-uptake by the plant after adding 5 t ha⁻¹ of air-dry sludge increased for a sludge with a high P/Fe weight ratio of 0.67, but decreased for a sludge with a low P/Fe ratio of 0.2. Increasing additions (0–15 t ha⁻¹) of the low-P/Fe sludge raised the P adsorption capacity of the soil linearly as soil-Fe_o rose. This indicates that ferrihydrite is the

main Fe oxide in the sludge. Sludges with low P should, therefore, not be amended with Fe salts (Römer and Samie, 2001; 2002).

Iron-rich waste material used for inactivating hazardous pollutants must be deposited in such a way that the pollutants do not re-enter the ecosystem. These materials are usually dumped as landfill or such like. The waste may be reduced in volume by incineration, town refuse being a common example of this. If Fe oxides contribute to the inactivation of the pollutants in the waste, their potential to retain them may drastically change (in/decrease) during this process. Model experiments were, therefore, carried out to study these changes using either model Fe oxides or Fe oxide-enriched waste material. For example, an air pollution control residue containing heavy metals retained by ferrihydrite was heated to 500 and 600 °C. This led to an (unwanted) volatilization of Hg and to an increased extractability of As, Cr and Mo with solvents with pH >7 and to that of Cd, Pb, Cu, Ni and Zn with extractants with pH <7. In contrast, Cr was immobilized at 900 °C through reduction to Cr^{III} (Sørensen et al. 2000). An accompanying model experiment with Pb-, Hg-, Cr- and Cd-ferrihydrite coprecipitates showed indeed that the metals were leachable when the ferrihydrite was transformed to hematite by heating (Sørensen et al. 2000a). Pb and Cd were also released when ferrihydrite transformed to goethite/hematite in an aqueous system at 40 and 70 °C and pH 6, whereas Mn and Ni were immobilized by structural incorporation (Ford et al. 1997); similar results were obtained by Cornell et al. (1992). Finally, ageing heavy-metal-ferrihydrite coprecipitates at RT for 200 d resulted in moderate stabilization of Zn and Cu, but not Cd and Pb. Heating at 70 °C for 60 d converted the ferrihydrite into hematite, and led to a drastic decrease in the solubility of Zn, Cd and Cu, but a strong increase in that of Pb (Martinez and McBride, 1998; Martinez et al. 1999).

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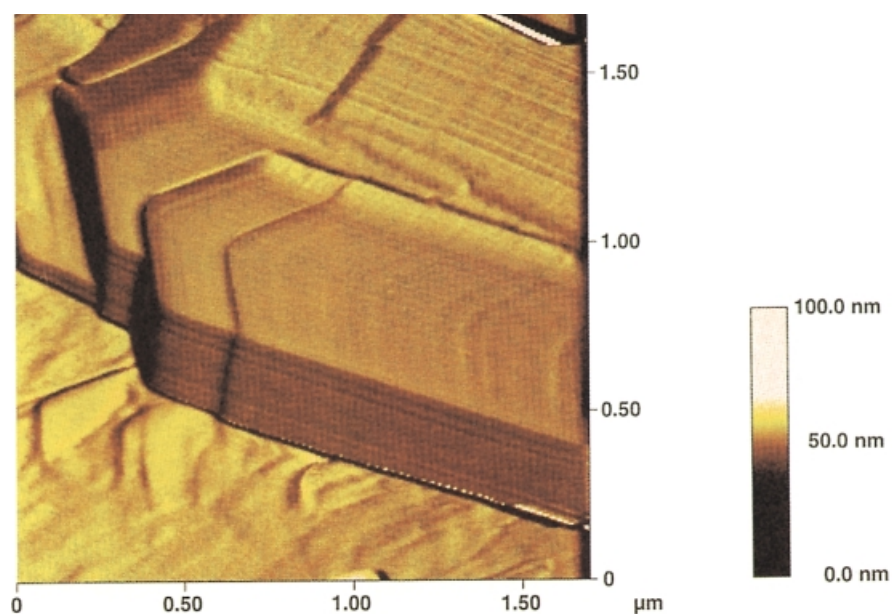


Plate 4.I Atomic force microscope image of a synthetic goethite crystal scanned in deflection mode (see Weidler et al., 1996, with permission, courtesy P. Weidler).

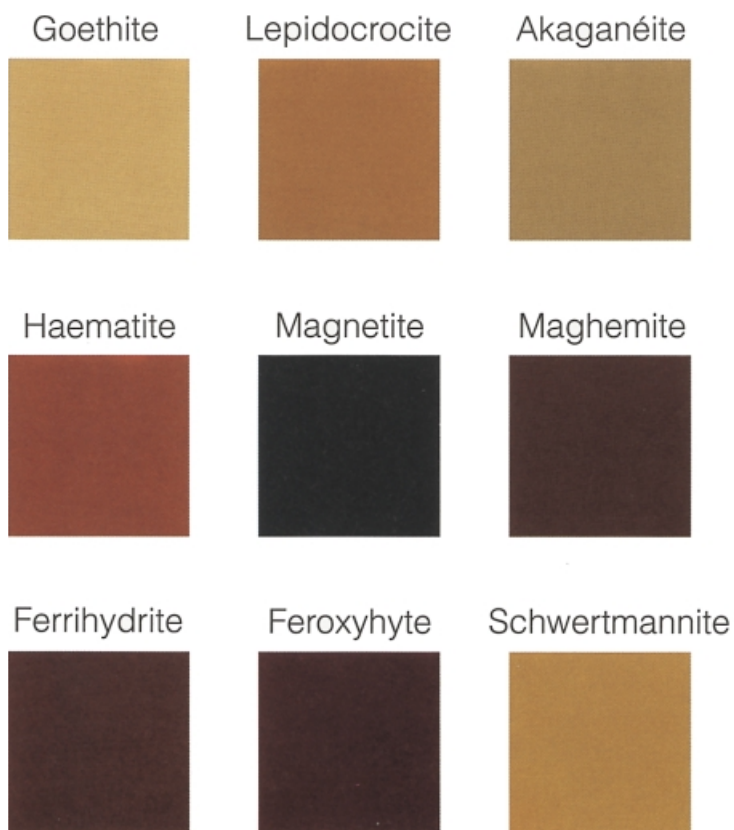


Plate 6.1 Colours of Fe^{III} oxides



Plate 6.II Effect of particle size and cation substitution on the colour of Fe^{III} oxides

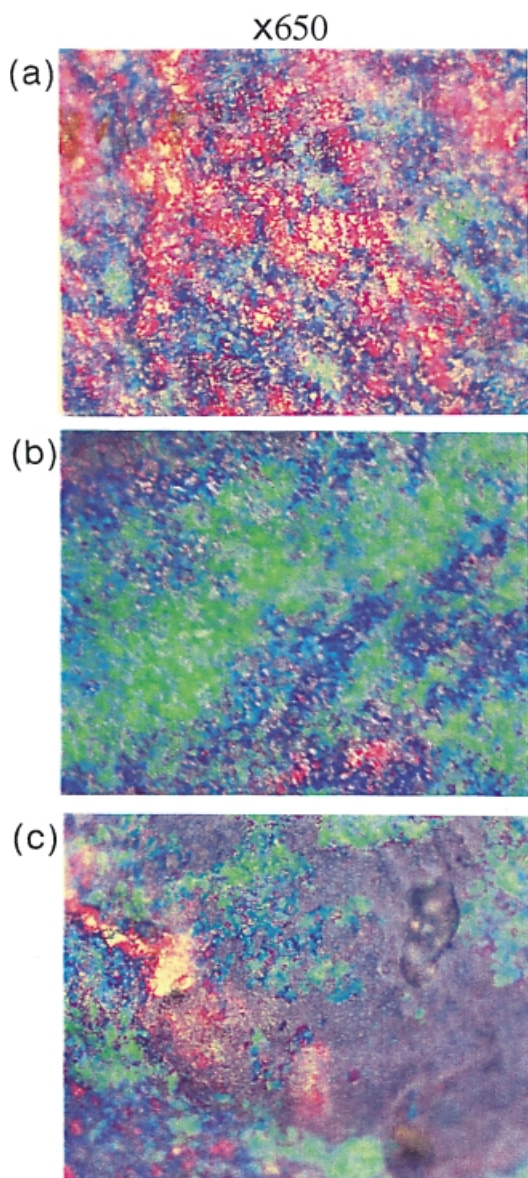


Plate 10.1 Optical microscope images of the iridescent regions on the surface of the dry β -FeOOH sol (x650) (Reprinted from Maeda & Maeda, copyright 1996. With permission and Courtesy, H. Maeda).

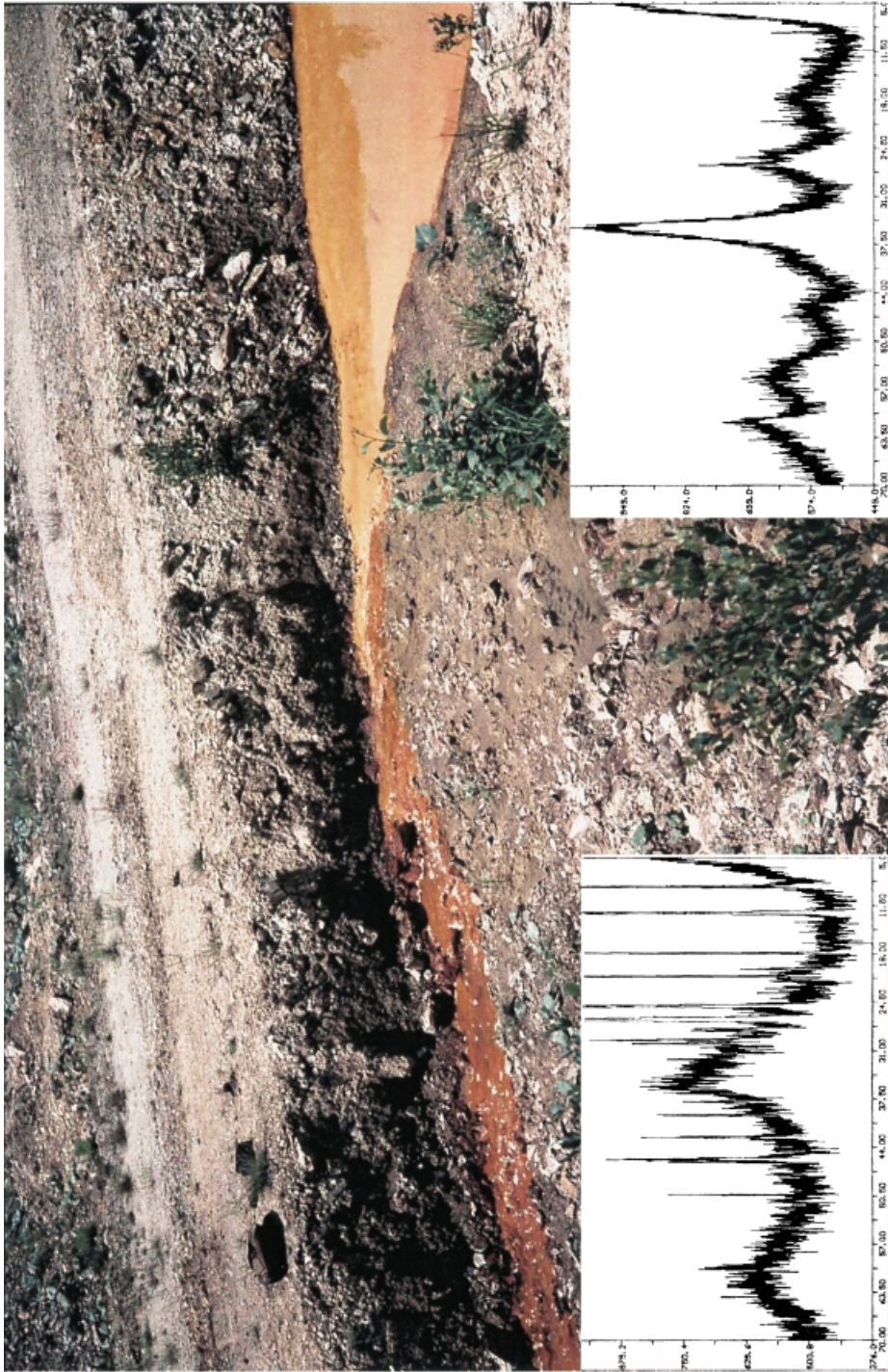


Plate 13.1 The colour changes of the ochreous precipitates formed from ferrous acid mine water from a lignite mine near Sokolov, Czech Republic, and their X-ray patterns clearly indicate the abrupt transition from schwertmannite at a water-pH of 3.7 on the right to 2-line ferrihydrite after neutralization by a pH 8.2-water on the left side (arrows) (Courtesy E. Murad; Murad & Rojik, 2003, with permission).

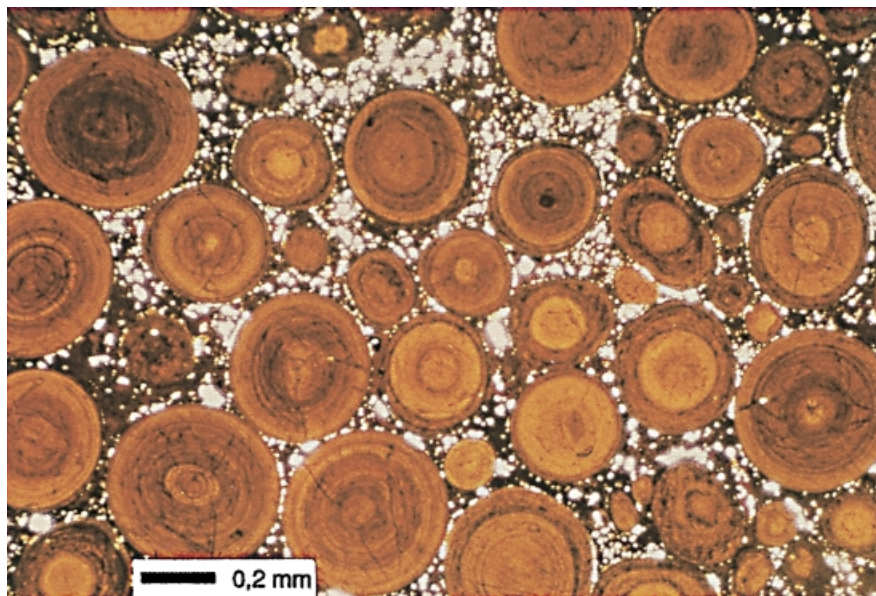


Plate 15.I Iron oxide ooids in a silty matrix from an iron oolite – a thin section. Fula, Sudan (Schwarz, 1992; Courtesy T. Schwarz).



Plate 15.II Iron oxide formation by atmospheric weathering of a pyrite vein in a limestone (photo courtesy, Ph. Jaesche).

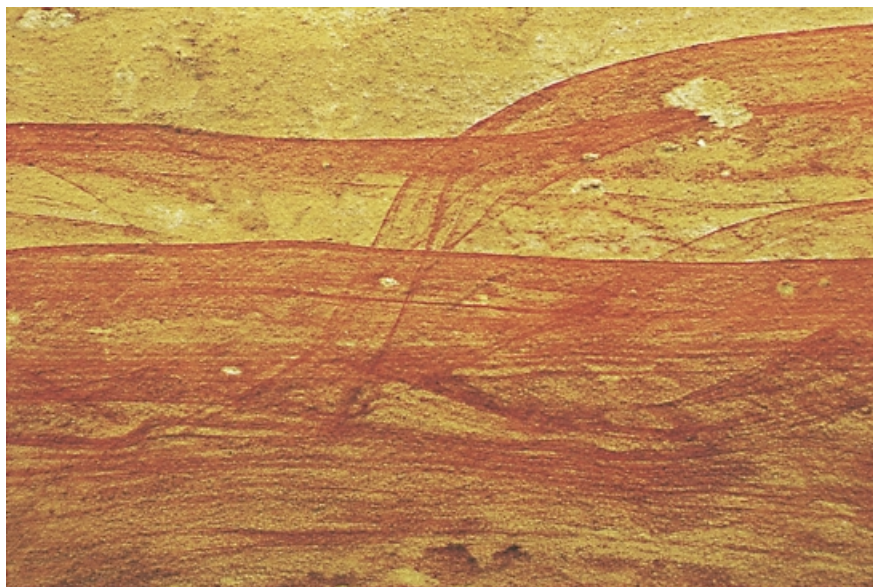


Plate 15.III Iron oxide bands in sandy-gravelly Pleistocene sediments, South Australia (Art object by Nicolaus Lang, courtesy H. Stanjek).



Plate 15.IV Ferrihydrite deposit of a ferriferous spring, Iceland (courtesy L. Carlson).



Plate 15.V Drain pipe clogged with ferrihydrite (courtesy H. Kuntze).

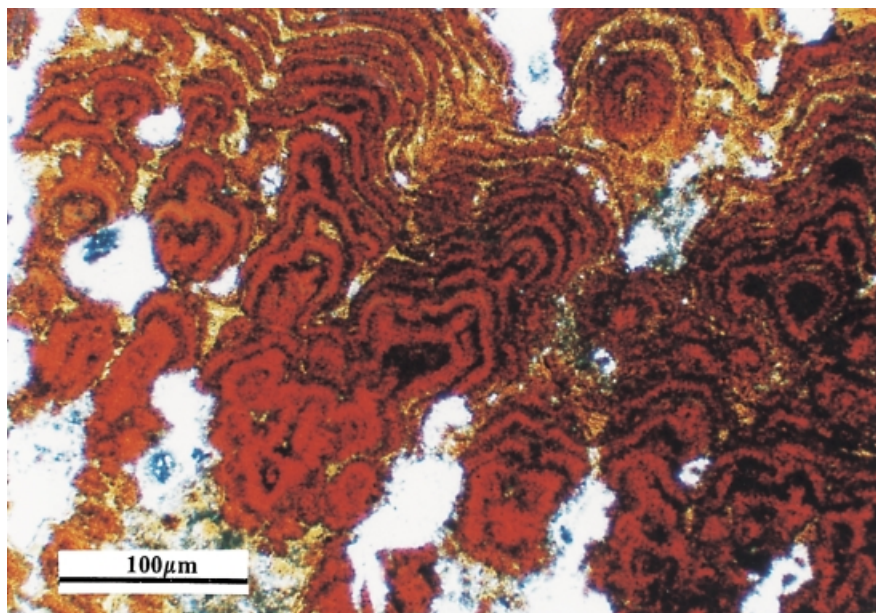


Plate 15.VI Rhythmic Fe oxide bioformation from a volcanic spring near Kyoto (Tazaki, 2000; with permission).



Plate 15.VII Acid mine water precipitate, Ohio
(courtesy J.M. Bigham).



Plate 15.VIII The surface of the red planet Mars. A planar area in the northern mid-latitude of Mars. The colour of the surface and the sky is primarily due to the ubiquitous presence of fine, red dust. The horizon is ca. 3 km away from the spacecraft (Viking Lander I) (courtesy NASA, Houston, Texas).



Plate 16.1 a) Soil profile coloured by goethite (Ochrept, France).
b) Soil profile coloured by hematite (Ultisol, Brazil). c) Soil profile
coloured by lepidocrocite (Aquept, South Africa). d) Ferrihydrite
formation by oxidation of Fe^{2+} in water seeping out of a Gley.



Plate 16.I e) Root channel in a gley soil stained by Fe oxide.
f) Bleaching of the surface layer of a red soil aggregate by microbial reduction of the hematite. See root mat at the aggregate's surface supplying the biomass.

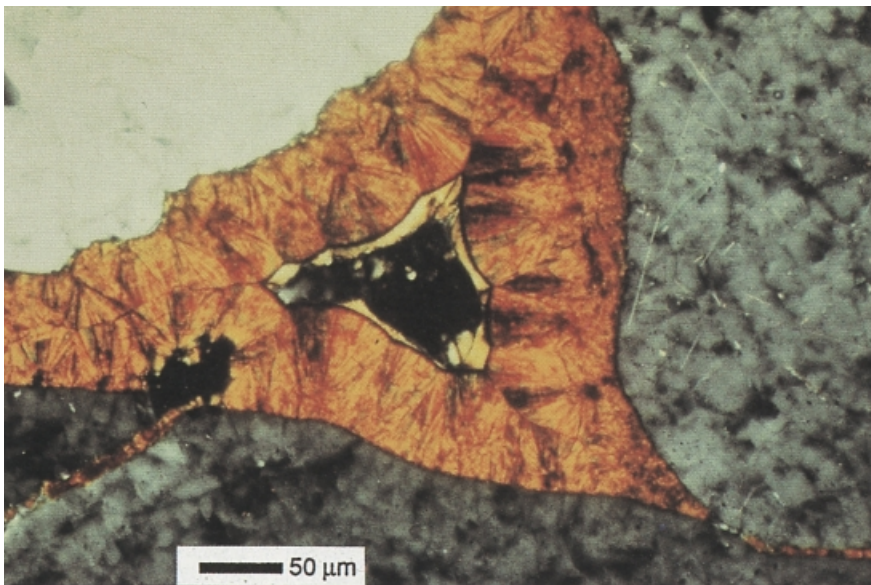


Plate 16.II Goethite "palisades" around quartz grains in a ferricrete. Debal, Sudan (Schwarz 1992; with permission; courtesy T. Schwarz)



Plate 16.III Highway on a hematite-coloured soil between Concepcion and San Ignacio de Velasco, Bolivia (Courtesy Dr. P. Schad).

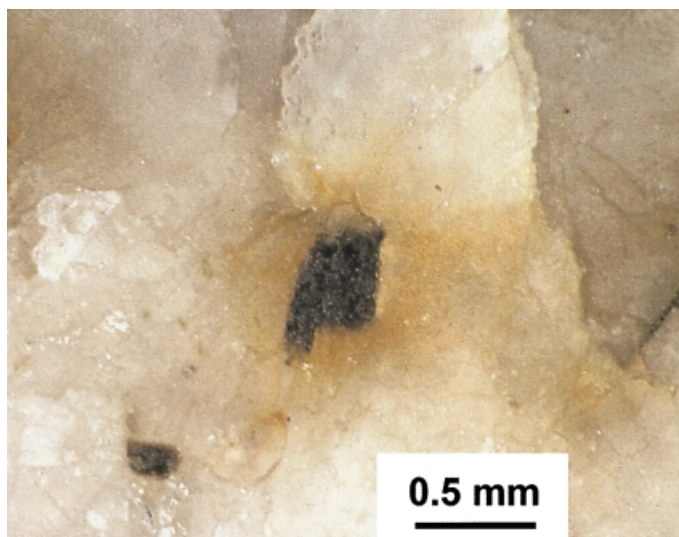


Plate 16.IV Biotite crystal surrounded by goethite and ferrihydrite in a weathered granite (Courtesy Dr. T. Nagano).



Plate 18.1 Rust formation on a window sill from a corroding iron screen (St. Philibert, Tournus, France, Courtesy H. Breuning)



Plate 18.2 Rusted mouse trap after ca. 2 years in a wet soil



Plate 19.I Iron oxide coloured mask, Ekoi, Nigeria (Courtesy, R. Miehler)



a



b

Plate 19.II Use of iron oxides as paints: a) Summer house of C. F. Lñne near Upsala, Sweden, painted with hematite produced by calcination of pyrite (Courtesy Mrs. D. Schwertmann).
b) House of the Lenbach Art Gallery, Munich, painted with goethite (Courtesy Dr. J. Friedel).



Plate 19.III Outcrop of natural Fe oxide (goethite, hematite) pigments at Luberon, France (Courtesy H. Stanjek)



Plate 19.IV a) Processing natural iron oxide pigments at Luberon, France (Courtesy J. Burlot).



Plate 19.IV b) Natural iron oxide pigments (Courtesy M. Sauveté).



Plate 20.I Industrial drying of haematite pigment
(courtesy Bayer AG, Krefeld, Germany).



Plate 20.II Industrial production of goethite pigment
(courtesy Bayer AG, Krefeld, Germany).